Vacancy-Induced Ferromagnetic Behavior in Antiferromagnetic NiO Nanoparticles: A Positron Annihilation Study

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Pure NiO nanoparticles were subjected to isochronal thermal treatments in open air from 100 to 1000 °C. X-ray diffraction (XRD) patterns indicate that all annealed samples exhibit a single phase of face-centered cubic (FCC) crystalline structure, obvious grain growth occurs only above 400 °C and the average crystallite size increases from 20 to 80 nm. X-ray photoelectron spectroscopy (XPS) shows that only very few amount of Ni2+ and no impurity element have been found in the annealed samples. Positron annihilation measurements reveal that large number of Ni-vacancy defects exist in the grain surface region. These surface defects begin to recover after annealing above 400 °C, and most of them are removed at 1000 °C. Room temperature ferromagnetism is obviously observed for the samples annealed at 100 and 400 °C. The saturation magnetization gradually decreases with the increase of the annealing temperature, and it almost disappears at 800 and 1000 °C. The disappearance of ferromagnetism shows good coincidence with the recovery of Ni-vacancies. Our results suggest that the anomalous ferromagnetic behavior in NiO nanoparticles might be due to the surface Ni-vacancy defects instead of grain size effects.

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Nanostructured antiferromagnetic (AF) materials have attracted much attention because of their promising applications in spin valves1 and next-generation magnetic random access memories (MRAM).2 It is well known that the bulk AF materials are magnetically compensated and have zero net magnetic moment in zero applied field, while fine particles of an AF material should display either weak ferromagnetism (FM) or superparamagnetism (SPM).3 Since Richardson and Milligan first reported anomalous magnetic properties in NiO nanoparticles,4 ferromagnetic behaviors were found in an increasing number of AF nanomaterials.5–4 However, the mechanism of these different magnetic properties remains debatable. Many mechanistic views have been proposed for the observed FM, such as surface and finite size effects,6–11 chemical valence change,12–15 superparamagnetic clusters,16 or vacancy relevant uncompensated surface spins.17 Consequently, it is important to investigate the magnetic mechanism of AF nanomaterials extensively.

Among the various nan structured AF transition metal monoxides, NiO has been widely investigated, because it is a unique metal-deficient p-type semiconductor presenting a wide band-gap (3.6–4.0 eV), and its bulk form possesses a relatively high Néel temperature \( T_N (523 \text{ K}) \). As a consequence, it can store high storage density of magnetic recording media due to allowing magnetic stability at very low volumes far above room temperature.17 In the recent few decades, great efforts have been devoted to exploring the unexpected magnetic properties in NiO nanomaterials, such as large magnetic moments, enhanced coercivity, spin glass freezing and hysteric loop shifts. However, up to now the underlying mechanism for the FM is still unclear. It has been reported that the FM might come from the surface and finite size effects, or a net magnetic moment probably arises from uncompensated spins. Several models, such as the two-sublattice model,7 multi-sublattice model,6 and core-shell model10,12–14,18–24 have been used to illustrate the anomalous properties of NiO nanoparticles. However, different groups reported that surface effects and size effects on the ferromagnetic properties of the nanomaterials are inconsistent, even controversial. Moreover, Bi et al.25 suggested that the ferromagnetic behavior of NiO nanocrystals was caused by the combined effects of the broken bonds and the lattice distortion. There are also other results stating that the ferromagnetic moments in AF NiO nanoparticles are attributed to the presence of inevitable metallic nickel clusters9 or higher oxidation state Ni3+ ions5,16 in NiO lattice. Richardson et al.16, however, have demonstrated that these moments only have a very slight change by oxidation (to eliminate Ni metal) or mild reduction (to eliminate Ni3+). Up to date, the most widely accepted mechanism is the vacancy induced FM for AF NiO nanomaterials.

The evidence of vacancy induced FM in nonmagnetic systems26,27 implies that vacancies also can play an important role in determining the ferromagnetic behavior of AF nanoparticles like CuO,28 Co3O4,29 and NiO,30,31 but it is still a highly controversial issue, as it is indistinguishable whether the FM is due to cation or anion vacancies effects. As for NiO nanomaterials, the exact origin of FM also remains unresolved, till now. Zhang et al.29 reported that the occurrence of half-metallic FM of NiO is due to singly or doubly negatively charged nickel vacancies. Mandal et al.30,31 proved that anomalous ferromagnetic properties in nanoscale NiO originate from Ni vacancies, and the distribution of vacancies can be deemed within a core-shell model.31 Especially, Sugiyama et al.32 discovered that well-aligned dislocations in AF NiO crystals could introduce unique ferromagnetic properties due to the local non-stoichiometry of the dislocation cores with Ni deficiency, i.e., Ni-vacancy. The ferromagnetic dislocations had high coercivity because of their strong interaction with the surrounding AF bulk phase. Yang et al.,33 on the other hand, suggested that the surface oxygen vacancy was the predominant contribution to the FM in NiO nanoparticles, and explained the larger \( H_C \) and exchange bias as a fixed effect between the AF core and the FM shell. Furthermore, Madhu et al.34 recently propose a credible model connecting the ferromagnetic interaction to the presence of both uncompensated surface O2− and Ni4+ vacancies, and confirm the ferromagnetic properties of NiO nanoparticles changing with the concentration of anion and/or cation vacan-
cies. These controversial results introduce the question which specific vacancy defect is the origin of FM in AF NiO nanoparticles? Particularly, if the type of vacancy is not successfully identified or remains disputed, the analysis of the FMs origin would be greatly unreliable.

Thus, it is necessary to clarify which specific vacancy defect is essential to induce the ferromagnetic behavior in AF NiO nanoparticles. Systematic experiments are needed to resolve the above problem, and a suitable method for the characterization of the surface vacancy defects in nanoparticles is also necessary. Positron annihilation spectroscopy has been proved to be a sensitive probe for the investigation of vacancy defects in solids.\(^35,36\) It is specifically useful in characterizing of vacancy defects on the surface of nanoparticles. This is because that the positron diffusion length \(L_d\) (typically about 100 nm) is usually longer than the nanograin radius. Therefore, almost all the positrons that are emitted into the grains will diffuse to the grain surface region and get trapped by vacancy defects on the surface.\(^37\) The positron annihilation parameters such as annihilation lifetime and Doppler broadening of annihilation radiation in vacancy trapped state are different from the defect free bulk state. The change of positron annihilation parameters at vacancy sites makes identification of vacancy defects rather sensitive and straightforward. In addition, since annealing is a suitable method to tune the proportion of point defects which affect magnetic properties, the presence of different vacancy defects in the annealed samples can be monitored and further mediated for FM manipulation by positron annihilation technique. In this paper, we studied the recovery process of surface vacancy defects in NiO nanocrystals during high temperature annealing by positron annihilation lifetime and Doppler broadening measurements. Variation of the ferromagnetic behavior of NiO nanoparticles was also studied. A good correlation between the FM and Ni-vacancy defects in the NiO grain surface region was observed, suggesting that the FM might originate from these defects.

Experimental

Samples for this study were pure NiO nanopowders with a grain size about 20 nm and purity of 99.9%, which were purchased from Beijing Nachen S & T Ltd. First, the nanopowders were pressed with 6 Mpa pressure for 1 min to get tablets, which had disk shape with a diameter of about 15 mm and thickness of about 1–2 mm. Then, the tablets were isochronally annealed in air from 100 to 1000 °C for a duration of 2 h at each temperature. Finally, the annealed tablets were naturally cooled down to room temperature. To avoid any magnetic contamination, we only used nonmagnetic tweezers and holders to manipulate the samples.

The crystalline structure and the phase of all annealed samples were characterized by X-ray diffraction (XRD) (Bruker D8 Advance) using the Cu Kα radiation and a Ni filter. The scanning rate was 1°/min with a step of 0.02° and the scanning range was from 20 to 90°. The chemical composition and element chemical status in NiO nanocrystals annealed were analyzed by X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi) performed using a monochromatic Al Kα radiation (1486.6 eV). The microstructure defects of all NiO nanocrystals after each annealing step were investigated by positron annihilation spectroscopy. A \(^{22}\)Na positron source with the activity of \(\approx 5 \mu\text{Ci}\) was sandwiched between two pieces of identical sample tablets for the measurements. Positron lifetime spectra (PLS) were measured using a fast-fast coincidence system which has a time resolution of about 220 ps. To ensure the repeatability of the measurements, two lifetime spectra were measured for the sample after each annealing. Coincidence Doppler broadening spectra (CDBS) were measured using two high purity (HP)-Ge detectors, which had energy resolutions of about 1.76 and 1.64 keV (FWHM) at 1.33 MeV, respectively. The two Ge detectors are put in the opposite direction perpendicular to the two lifetime detectors. The Doppler spectra were characterized by the S and W parameters, which are calculated from the ratio of the low momentum \((511 \pm 0.68 \text{ keV)}\) area and the high momentum \((511 \pm 2.86 \text{ keV to } 511 \pm 5.73 \text{ keV})\) area to the total area of the \(511 \text{ keV}\) annihilation peak, respectively. The PLS and CDBS were measured simultaneously. About \(1 \times 10^6\) and \(4 \times 10^6\) total counts were collected for each lifetime and Doppler spectrum, respectively. Magnetic properties were measured by using vibrating sample magnetometer (VSM) of physical property measurement system (Quantum Design, PPMS). All the above preparations and measurements were performed at room temperature.

Results and Discussion

\textbf{XRD characterization.—}Fig. 1 displays the X-ray diffraction (XRD) spectrum of NiO nanocrystals after annealing at temperatures of 100, 400, 600, 800, and 1000 °C for 2 hours. All the observed diffraction peaks for each sample annealed at different temperatures agree well with the standard values (JCPDS Card No 04-0835). It can be seen that all the annealed samples exhibited characteristic diffraction peaks corresponding to the (111), (200), (220), (311), and (222) planes of the face-centered cubic (FCC) crystalline structure, and no impurity phases were observed. As the annealing temperature rises from 100 to 1000 °C, the characteristic peaks become very sharp, and no phase transition was observed. Therefore, XRD patterns confirmed that all the annealed samples were of polycrystalline structure and single phase. It is also shown in Fig. 1 that with the increase of annealing temperature, the intensity of the observed diffraction peaks increases and the width of the peak decreases, which suggests a possible increase of the grain sizes. The average crystallite sizes of the annealed NiO samples are calculated using the Debye-Scherrer’s formula: \(^38\)

\[
D_{abh} = K \lambda / \beta \cos \theta, \tag{1}
\]

where \(D_{abh}\) is the average grain size perpendicular to the \((hkl)\) plane, \(K\) is the shape factor (usually taken as 0.89), \(\lambda\) is the X-ray wavelength of Cu Kα radiation \((\lambda=0.15418 \text{ nm})\), \(\beta\) is the FWHM of the XRD peak (ever observed peak in the spectra was fitted with a Gaussian function), and \(\theta\) is the Bragg angle. Fig. 2 shows the variation of average grain size with annealing temperature for NiO nanocrystals. In the annealing temperature interval between 100 and 400 °C, the average grain size of the NiO nanoparticles is estimated to be about 20 nm. As the annealing temperature increases from 500 to 1000 °C, the average grain size increases continuously from 23 to 80 nm. Obviously the grain begins to grow above 400 °C and grows faster at about 500 °C.

\textbf{XPS analysis.—}Fig. 3a shows XPS survey spectra of NiO nanocrystals annealed at 100, 400, 600, 800, and 1000 °C, respectively. The characteristic peaks of Ni, O and C are present in the XPS survey spectra against binding energy, which indicate that three
elements, Ni, O and C are detected and the various XPS peaks are labeled accordingly. But no impurities such as Fe, Co etc. were found in all annealed samples. The carbon peak was likely from the residual carbon of the samples and adventitious hydrocarbon of XPS instrument.

In order to analyze the valence state and chemical environment of the Ni element in NiO nanocrystals, Fig. 3b shows the comparison of XPS spectra of Ni 2p of all annealed samples. The binding energies at ~853.5 and ~872.4 eV were attributed to the 2p3/2 and 2p1/2 peaks of Ni2+ in NiO nanocrystals, respectively. The peaks at ~860.6 and ~878.9 eV were due to the satellite peaks of 2p3/2 and 2p1/2 peaks of Ni2+, respectively. In addition, a weak splitting peak of Ni 2p3/2 peak was also observable at ~855.3 eV, which is due to the presence of oxidation state of Ni3+. But the above XRD measurements show that no any other impurity phases were observed in all annealed samples within the detection limit of X-ray diffractometer. This indicated that there are only very few amount of Ni3+ ions in NiO nanocrystals, which are hardly detected by XRD. One possible explanation was that Ni2+ on the surface of NiO nanocrystals is easily oxidized into Ni3+ in open air from 100 to 1000 °C, or Ni2O3 may exist in the primary samples. However, as the annealing temperature increases from 100 to 1000 °C, all the observed peaks did not change obviously in XPS spectra of Ni 2p. According to the previous reported data, the electron binding energy of Ni 2p3/2 is about 851.7–853 eV for Ni metal, 853.6–855.5 eV for NiO, and 855.8–856 eV for Ni2O3. Comparing our results with these data, we could deduce that only a very small amount of Ni2O3 is present, but Ni metal does not exist in the present NiO samples annealed from 100 to 1000 °C.

**Positron annihilation measurements** — The microstructural defects in NiO nanocrystals annealed at different temperatures were studied by positron lifetime measurements. Using the PATFIT program, all the lifetime spectra are evaluated to three lifetime components named as τ1, τ2 and τ3 in the samples annealed at lower temperatures. Their corresponding relative intensities are I1, I2 and I3, respectively. These results reveal useful information about the defect structure of the annealed NiO samples. It was reported that positron bulk lifetime τb in NiO single crystals is approximately 150 ps by either experimental measurement or theoretical calculation. VNi is an effective positron trap, and Creamer et al. observed the positron lifetime in nickel monovacancies (VNi) to be about 210 ps. While VO is positively charged, therefore it is not likely to trap positrons. For our NiO nanocrystals annealed at 100–400 °C, the shortest lifetime τ1 is about 240 ps, and the intermediate lifetime τ2 is around 420 ps. Apparently, τ1 is longer than the bulk lifetime τb and close to the lifetime of positrons trapped in monovacancies (VNi), so this indicates that τ1 comprises positron lifetime trapped at VNi. As τ2 is much longer than τ1 and τ3, and the ratio τ2/τ3 is 2.8, using τ3 of about 150 ps, this corresponds to the positron lifetime in larger vacancy clusters according to theoretical calculations. Therefore, τ3 is obviously due to positron trapping by Ni-related vacancy clusters. In our samples, all these Ni-vacancy defects revealed by τ1 and τ3 are usually distributed in the grain surface and boundary region. However, the longest lifetime τ2 is about 2.1–7.4 ns, which suggests positronium formation in microvoids among close packed nanoparticles. τ3 is clearly the o-Ps annihilation lifetime, which is related to the size of the microvoids due to the pick-off annihilation with the electrons at the void wall. Fig. 4 displays the longest positron lifetime component τ3 and its relative intensity I3 versus annealing temperatures. As shown in Fig. 4, I3 is
The relative intensity $I_1$ and $I_2$ of NiO nanocrystals after annealing at different temperatures.

relatively small (5.4%) and decreases drastically to as low as 0.2% after annealing at low temperature of 200°C. Therefore, we will not discuss further this long lifetime in the following study.

As for the point defect structure of NiO, it has been investigated earlier with different experimental techniques including thermogravimetry,\textsuperscript{47} electrical conductivity,\textsuperscript{48,49} and perturbed angular correlation spectroscopy.\textsuperscript{50} Thus, there is a general agreement that the primary point defects in NiO are metal vacancies.\textsuperscript{30,51} Zhang et al.\textsuperscript{29} investigated stability and magnetism of vacancies in NiO using the GGA+U First-principle computation method, and they found that Ni vacancy is the predominant defect and the doubly ionized cation vacancy is the most stable defect under oxygen-rich conditions. From the literature,\textsuperscript{30,48} we also see that the Ni vacancy could be in singly, doubly, or mixed charge states in the case of NiO. However, the positrons are only trapped within the non-stoichiometric vacancy defects like Ni-related vacancies or their clusters (such as $V_{Ni}$, $V_{Ni+O}$, $V_{Ni+Ni}$, $V_{Ni+O+Ni}$, etc.), because they are negatively or neutral charged and thus can attract positrons. Therefore, our positron annihilation results are consistent with previous experimental results.\textsuperscript{30,51}

Fig. 5 shows $\tau_1$, $\tau_2$ and the corresponding intensities ($I_1$, $I_2$) in the NiO nanocrystals annealed at different temperatures. $\tau_1$ keeps nearly constant at about 240 ps after annealing up to 500°C. With increasing annealing temperature, it starts to slowly decrease and drops to around 150 ps at 800°C which practically reaches the bulk lifetime in NiO single crystals.\textsuperscript{43-45} and then remains almost constant up to 1000°C. This implies that the surface vacancy defects begin to recover at about 500°C and most of them have been removed at 800°C as $\tau_1$ decreases to virtually the bulk value in NiO single crystals. The relative intensity $I_1$ shows a notable increase at about 400°C. As for $\tau_2$, it has no obvious change below an annealing temperature of 400°C. This suggests that annealing from 100 to 400°C has no impact on the vacancy clusters. After annealing at above 400°C, $\tau_2$ begins to slowly decrease, which reveals that the vacancy clusters shrink increasingly. The relative intensity $I_2$ also displays apparent decrease above 400°C. The reason for the reduction of $I_2$ can be due to the smaller fraction of positrons annihilation at the surface and interface region. This also probably indicates recovery of the vacancy clusters. Eventually, $\tau_2$ and $I_2$ decrease respectively to 200 ps and 1% after annealing at 1000°C, which make clear that most of the vacancy clusters may have been annealed out. However, it is not enough to analyze only the decomposition results of the positron lifetime spectra. We also need to consider the average positron lifetime $\tau_{1,2}$ calculated from $\tau_1$ and $\tau_2$, which reflects the overall information about the vacancy defects. Fig. 6 presents the variation of average positron lifetime $\tau_{1,2}$ as a function of the annealing temperature for NiO nanocrystals. It can be seen from Fig. 6 that $\tau_{1,2}$ also starts to slowly decrease at above 400°C and drops from 300 ps to about 150 ps after annealing at 1000°C, which indicates that the surface vacancy defects in the grain boundary region disappear slowly after annealing from 400 to 1000°C.

As a further support to above analysis of defects, the Doppler broadening $S$ parameter and $W$ parameter were also measured. Fig. 7a shows the $S$ parameter as a function of annealing temperature. The $S$ parameter first has a very slight decrease at annealing temperature from 100 to 400°C, then decreases gradually after annealing up to 1000°C. The decrease of $S$ parameter reveals a decreasing annihilation probability of positrons with the lower momentum valence electrons, suggesting that the vacancy concentrations in the sample decrease with the increase of annealing temperature. This indicates continuous recovery of vacancy defects after annealing. Fig. 7b displays the variation of $S$ parameter versus $W$ parameter during annealing process. The $S$-$W$ plot provides additional information on the change of defect species. All the data points in Fig. 7b were almost centered on
a straight line, implying that there is no change of the defect species during annealing. Therefore, it is also concluded from Figs. 7a and 7b that annealing up to 1000 °C causes a gradual decrease of the surface vacancy concentration.

The above positron annihilations results indicate that the surface vacancy defects in NiO nanocrystals start to recover gradually after annealing above 400 °C, and most of them are annealed out at 1000 °C. However, XRD measurements show that the NiO grain size has obviously grown up to 80 nm after annealing from 400 to 1000 °C. The increase of grain size may be another reason for the decrease of the positron lifetime and Doppler broadening S parameter during annealing, since the grain growth will lead to decrease of the fraction of interface region, so that a smaller number of positrons will diffuse out of the grain and annihilate in the grain boundary region. However, even though the NiO grain diameter increases to about 80 nm after annealing at 1000 °C, the grain radius is still less than the positron diffusion length \( L_d \) (typically about 100 nm) in solids. Thus, almost all the positrons emitted into the NiO grains will still diffuse toward the grain boundaries and get trapped by surface vacancies. In other words, the fraction of positrons annihilating in the grain surface will not be affected. Therefore, the decrease of the positron lifetime and Doppler broadening S parameter after annealing should be primarily owe to the recovery of the surface vacancy defects.

**Ferromagnetic behavior.**—Fig. 8 shows the magnetization versus applied magnetic field (M-H curves) for the annealed samples at room temperature. It is seen that hysteresis loops can be clearly observed in the M-H curves of the NiO nanoparticles annealed at 100 and 400 °C, which indicates room temperature ferromagnetism in these annealed samples. Interestingly, the magnetization value decreases with increasing annealing temperature. The nature of the M-H curves displays gradual disappearance of the hysteresis loops with increase in the annealing temperature, which manifests that the ferromagnetism becomes much weaker with the increase of annealing temperature from 100 to 1000 °C.

As shown in Fig. 8, these loops are extremely similar to the characterizations in Refs. 10, 20–22,24. Especially, the magnetization of NiO nanoparticles annealed at 1000 °C exhibits nearly linear response to the applied magnetic field in the range of up to 50 kOe. In addition, the loop passes through the origin with no remnant magnetization (\( M_r \)) and coercivity (\( H_c \)). This confirms the presence of antiferromagnetism (AFM) in the annealed samples, similar to the bulk NiO. On the other hand, for the NiO nanoparticles annealed at low temperatures of 100 and 400 °C, during the initial magnetization process, the magnetization increases with increasing applied field in the lower-field region, but the increase of magnetization weakens as the applied field further increases. Finally, the magnetization increases almost linearly with increasing magnetic field, and does not saturate in the high-field region. These observations suggest that the magnetization consists of two possible components: an easily magnetizing component in the low-field region, and a non-saturating component responsible for the nearly linear variation at the high-field region.23,22 Thus, two magnetic phases are assumed to be associated, one with AFM and another with FM. The non-saturating nature of the loops implies the existence of an AF phase. So, if we subtract this AF contribution from the overall magnetic behavior, we will extract the other phase. As done previously,21,24 we obtain the saturation magnetization (\( M_s \)) in the same way. For the NiO nanoparticles annealed at 100 and 400 °C, after subtracting the AF contribution, the saturation magnetization is about 0.168 emu/g and 0.12 emu/g, respectively. Finally, the FM becomes very weak after annealing at 600 °C, and the saturation magnetization decreases to about 0.01 emu/g. Thus, Fig. 9 shows that the value of saturation magnetization \( M_s \) decreases gradually with increasing annealing temperature.

Our positron annihilations results reveal that a numerous population of vacancy defects locates at the grain surface and interface region in all NiO nanoparticles annealed at low temperatures, and the recovery process of defects is well consistent with the variation of FM as the annealing temperature rise from 100 to 1000 °C. However, XRD confirms that the grain size increases with the annealing temperature rising from 400 to 1000 °C. It is a general trend that the magnetization becomes weaker with increasing grain size and disappears when the nanocrystals are transformed into bulk samples through sintering.26 As for NiO, Rinaldi-Montes et al.23–24 reported on how the antiferromagnetism of a bulk material can be broken when reducing its size under a given threshold. In our study, however, the RT FM of NiO nanoparticles decreases with an increase of grain size, possibly due to the decrease of vacancy defect concentrations at the surfaces of nanoparticles, which is supported by our positron annihilation measurements. Thus, it can be deduced that the FM has almost no correlation with the grain size, but would rather be attributed to vacancy defects on the surface of NiO nanoparticles. Therefore, the possible origin of FM associated with surface vacancy defects will be discussed in this study. The magnetization shows slight decrease after annealing up to 400 °C, while the average positron lifetime and S parameter also have a slight decrease. Further annealing causes recovery of the defects in the interface region, and the magnetization also becomes weaker. After annealing at 800-1000 °C, most of the defects have been removed, and the FM becomes weaker and finally invisible. Thus, a good correlation between ferromagnetic behavior and surface vacancy defects can be observed. Fig. 10 illustrates the saturation magnetization versus S parameter for NiO nanoparticles after annealing at 100, 200, 400, 600, 800 and 1000 °C. As the annealing temperature gradually rises from 100 to 1000 °C, the saturation magnetization decreases with decreasing S-parameter, which indicates further that the ferromagnetism

![Figure 8. M-H curves for NiO nanocrystals annealed at 100, 400, 600, 800 and 1000 °C.](image1)

![Figure 9. Saturation magnetization as a function of annealing temperature for NiO nanocrystals.](image2)
is well correlated with vacancy defects. Therefore, it can be inferred that the FM has been induced by vacancy defects on the surface of nanoparticles. According to above positron annihilation analysis, the possible vacancy defects might be Ni-related vacancies, since the oxygen vacancy is invisible to positrons. These Ni vacancies may play significant roles in producing FM, e.g. by polarizing the surrounding ligand atoms of the vacancy to form a localized magnetic moment. The ferromagnetic interaction between two localized moments induces a collective ferromagnetic behavior. From our results it has also been shown that a minimum concentration and the negative or neutral charge state of the vacancy defects are necessary to establish such collective ferromagnetic behavior in our NiO system.

The above result is supported by theoretical predictions of FM in NiO. Zhang et al. reported that half-metallic FM of NiO originates from singly or doubly negatively charged nickel vacancies. There are several experimental works which also confirm the Ni-vacancy induced FM in NiO nanoparticles. For example, Mandal et al., demonstrated that the anomalous ferromagnetic properties in nanoscale NiO is due to Ni vacancies on the surface of nanograins, and the observed ferromagnetic enhancement in NiO nanoparticles is not a true nanoscale effect but, rather, is mainly determined by the surface vacancy defects. Also, vacancy induced FM in other AF nanoparticles has already been indicated in the literature.

As for the origin of FM in NiO nanocrystals, it was also suspected to result from the presence of metallic Ni clusters or Ni$^{+}$ ions or impurity ferromagnetic phases in NiO lattice. However, the above XRD and XPS results indicate that there is no trace of metallic Ni, or any other ferromagnetic impurities such as Fe, Co etc in our samples within the detection limit of the two techniques. In addition, XPS spectra show that there are very few amount of Ni$^{+}$ ions in the NiO nanocrystals. But, Richardson et al. had verified that the presence of Ni$^{+}$ ions in NiO nanoparticles does not contribute to the observable ferromagnetic moment. Therefore, we can conclude that Ni-related vacancy defects induced RT FM in AF NiO nanocrystals. Further experiments are still needed, however, to clarify the exact Ni-related vacancy defect species that bear responsibility for the FM in NiO nanoparticles.

Conclusions

In conclusion, we have studied the microstructure and magnetic properties of NiO nanocrystals annealed in open air from 100 to 1000°C. X-ray diffraction (XRD) patterns indicate that all the annealed samples possess a simple phase of face-centered cubic (FCC) structure. The grain size was estimated from X-ray diffraction line using the Debye-Scherrer’s formula. The grain size shows obvious increase after annealing above 400°C and reaches about 80 nm at 1000°C. X-ray photoelectron spectroscopy (XPS) shows that there are only very few amount of Ni$^{+}$ and no other impurity phases in the annealed samples. Positron annihilation measurements reveal that large number of Ni-vacancy defects exist in the grain surface region. These defects begin to recover after annealing at above 400°C, and most of them are removed after annealing up to 1000°C. Room temperature ferromagnetism was obviously observed for the sample annealed at 100 and 400°C. The magnetization becomes very weak after the nanocrystals are annealed at 600°C, and it virtually disappears at 800 and 1000°C. The decrease of ferromagnetic contribution upon annealing shows good coincidence with the recovery of Ni-related vacancies, which induces the decrease in the number of magnetic moments and thus the effective magnetization. Thus, it can be concluded that the intrinsic ferromagnetism in our NiO nanocrystals is mostly related to the surface Ni-related vacancy defects rather than grain size effects.

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Figure 10. Saturation magnetization versus S-parameter for NiO nanocrystals after annealing at 100, 400, 600, 800 and 1000°C.
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