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Non-magnetic impurity induced magnetism in rutile TiO$_2$:K compounds

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Abstract

Recent ab initio studies have theoretically predicted room temperature ferromagnetism in several oxide materials of the type AO$_2$ in which the cation A$^{4+}$ is substituted by a non-magnetic element of the 1 A column. Our purpose is to address experimentally the possibility of magnetism in Ti$_{1-x}$K$_x$O$_2$ compounds. The samples have been synthesized via the solid state route method at equilibrium. Our study has shown that Ti$_{1-x}$K$_x$O$_2$ is thermodynamically unstable and leads to a phase separation, in contradiction with the hypothesis of ab initio calculations. In particular, the crystalline TiO$_2$ grains appear to be surrounded by K-based phase. The oxidization state of the Ti ion is found to be in Ti$^{4+}$ as confirmed from the x-ray photoelectron spectra measurement. Nevertheless, K:TiO$_2$ compounds exhibit weak paramagnetism with the highest magnetic moment of $\sim 0.5 \mu_B$ K$^{-1}$ but no long-range ferromagnetic order. The observed moment in these compounds remains much smaller than the predicted moment of 3 $\mu_B$ by ab initio calculation. The apparent contradictions between our experiments and first-principles studies are discussed.

(Some figures in this article are in colour only in the electronic version)
theoretical report predicting the surface magnetism in C doped SnO$_2$ [15]. Experimentally, room temperature (RT) ferromagnetism has been claimed in alkali metal doped ZnO [16–18]; Cu doped TiO$_2$ prepared in thin film [19, 20], and carbon doped TiO$_2$ prepared by the solid state route [21]. Recent experimental measurement of a magnetic moment of 0.2 $\mu_B$/K/ion in K:SnO$_2$ alloys by our group [22] extended the possibility of $d^0$ magnetism to cases where non-magnetic ions are not located at the substitution sites assumed in \textit{ab initio} studies.

The search for a suitable oxide, the appropriate non-magnetic dopant, and the optimal preparation procedure to obtain RT ferromagnetism is really intense but, in most cases, preparation of materials is not very well controlled. The inconsistencies and controversy may arise from the poor characterization of the samples, including stoichiometry, homogeneity, phase segregation, etc. For thin films, the stoichiometry and phase purity could be difficult to establish and the metastable preparation conditions likely result in phase segregation. It is therefore imperative to prepare bulk materials at equilibrium conditions, which will intrinsically diminish the uncertainties and inaccuracies in characterization. TiO$_2$ is a transparent wide bandgap material, with applications in photocatalysis, solar cells, semiconducting gas sensors, and as building blocks for photonic crystals. It is known to have two common symmetry forms, i.e. anatase and rutile structures. The possibility of ferromagnetism in TiO$_2$ by doping with a non-magnetic K element has not been investigated experimentally yet. We have prepared Ti$_{1-x}$K$_x$O$_2$ compounds ($0 \leq x \leq 0.06$) by the standard solid state route method by using high-purity TiO$_2$ (purity, 99.995%) and K$_2$CO$_3$ (99.999%) compounds. The maximum amount of any kind of trace magnetic impurities in the starting materials was found to be less than 0.9 ppm (parts per million) as mentioned by the supplier’s chemical analysis report. The final annealing in pellet form was carried out at 1200 °C for 30 h in air. Slow scan powder x-ray diffraction (XRD) patterns were collected by using a Philips XRD machine with Cu Kα radiation. Recording of microstructure images and elemental analysis have been carried out using a Zeiss-Ultra scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS). The x-ray photoelectron spectra (XPS) were recorded with a CLAM 4 vacuum generator (Al K line at 1486.6 eV) and the photoelectrons were collected at a pass energy of 20 eV in the fixed analyzer transmission mode. Magnetization ($M$) measurements as a function of magnetic field ($H$) and temperature ($T$) were carried out using a commercial SQUID magnetometer (Quantum Design, MPMS).

The XRD patterns for all K:TiO$_2$ samples are shown in figure 1. All the diffractions peaks could be indexed on the basis of the tetragonal rutile-type structure. No extra diffraction peaks were detected, showing that no crystalline parasitic phases are present in the samples within the limit of XRD. However, the refinement of x-ray patterns with the Fullprof program [23] reveals no significant change in the crystallographic lattice parameters, in comparison to pure TiO$_2$, upon doping (the lattice parameters for pure TiO$_2$ were found to be $a = b = 4.5945$ Å and $c = 2.9586$ Å, and they are comparable to those reported by Fleischhammer \textit{et al} [24]) showing that K ions do not substitute Ti ions. This can be understood by the large difference between the ionic radii of the six-coordinate Ti$^{4+}$ (0.61 Å) and that of K$^+$ (1.38 Å). To understand the microstructure, we have performed observations by high resolution SEM coupled with EDS. One typical SEM image of K:TiO$_2$ with 2 at. of K is shown in figure 2. It shows conglomerates of micrometric grains with sizes of 10–30 $\mu$m. The grain size is found to increase for higher K concentration of K:TiO$_2$ compounds. The determination of the chemical composition with the energy-dispersive analysis of x-rays (EDX) reveals the presence of K concentration close to the sample nominal concentration. Thus from the x-ray and SEM analyses, we can conclude that the compounds consist of crystalline TiO$_2$ grain-cores coated with a K-based phase. This could be understood on the basis of no detection of secondary phase in XRD, no change of crystallographic parameter in TiO$_2$, and K detection in elementary EDS analysis.
The oxidation states of titanium were analyzed via XPS (figure 3) in the K:TiO$_2$ compounds for K = 0, 0.04, and 0.06% compounds. The binding energies are referenced to the C 1s (284.8 eV) core level to compensate for any possible electrostatic shifts caused by charging of the samples during photoelectron measurements. In the pure TiO$_2$ sample, the Ti 2p peaks were found at 459.02 and 464.65 eV with a spin–orbital doublet splitting ($\Delta = \text{Ti} 2p_{3/2} - \text{Ti} 2p_{1/2}$) of 5.63 eV and an intensity ratio of 0.29 between the Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ in agreement with the literature results for the energy of Ti$^{4+}$ in clean TiO$_2$ [25]. With the K doping, a slight shift of the Ti (2p) peaks toward lower binding energies is observed. Compared with the energy of the Ti 2p$_{3/2}$ in the pure TiO$_2$, we observed a shift of about 0.06 and 0.61 eV for K = 0.04 and 0.06% samples, respectively. This effect cannot be ascribed to a change of the oxidation number of the titanium ions since the peak separation between Ti$^{4+}$ and Ti$^{3+}$/Ti$^{2+}$ is higher than 1.5 eV. Moreover, no broadening of the peaks and no shouldering peaks arise when increasing the K content. However, we cannot completely rule out the appearance of any kind of oxygen vacancies [27] (undetectable). However, the magnetization for the 2% K doped sample (figure 4(a)) increases almost ten times, in comparison to the magnetic moment observed for TiO$_2$. The magnetization values approach saturation with a maximum value of $\sim 0.048$ emu g$^{-1}$ (0.04 $\mu_B$/K) for the 2% K doped sample at 3 K, and it decreases down to $\sim 0.027$ emu g$^{-1}$ (0.01 $\mu_B$/K- samples to guarantee the reproducibility of results. The $M$–$H$ measurement for the TiO$_2$ compound shows that it exhibits weak paramagnetic behavior with a value of 0.005 emu g$^{-1}$ at 3 K and at 5 T field. This behavior is probably due to a very small fraction of localized unpaired 3d electrons of Ti$^{3+}$ [26] or of oxygen vacancies [27] (undetectable). However, the magnetization for the 2% K doped sample (figure 4(a)) increases almost ten times, in comparison to the magnetic moment observed for TiO$_2$. The magnetization values approach saturation with a maximum value of $\sim 0.048$ emu g$^{-1}$ (0.04 $\mu_B$/K) for the 2% K doped sample at 3 K, and it decreases down to $\sim 0.027$ emu g$^{-1}$ (0.01 $\mu_B$/K-
versus $T$ on the right side of this plot to determine order to be more accurate, we first used the high temperature $\chi$ determined from the fitted Curie constant $C$ in order to almost linear, suggesting the whole range of measured temperatures. However, the plot in figure 4(c). All samples display paramagnetic behavior in function of temperature, measured in a field of 0.02 T is shown with a maximum between 0 and 2%. The susceptibility as a magnetization of the samples, though not in a regular fashion relation $\mu_0$ with the temperature ($\approx 3\sqrt{3}k_B$) allows one to obtain the Curie constant ($C$) and Curie–Weiss measurement ($\theta$) directly from the inverse slope and intercept with the $T$-axis. The effective paramagnetic moment, $\mu_{\text{eff}}$ was determined from the fitted Curie constant $C(x)$ by using the relation $\mu_{\text{eff}} = \sqrt{3k_B/C(N\mu_0\mu_B^2)}$ with $C(x) = xC_0$ and all these parameters are given in table 1. The corresponding $x_0$ value increases regularly with the content of K. Non-zero $\theta_p$ is likely to be associated with the onset of magnetic interactions induced by K.

Let us now discuss the existing theoretical study for K doped TiO$_2$ [13]. In [13], a large magnetic moment of 3 $\mu_B$, comparable to that obtained in other samples of K and Na doped ZrO$_2$ [5], has been predicted. In the ab initio studies one assumes a real substitution of Ti$^{4+}$ by K$^+$. The essential point is that thermodynamics is ignored in ab initio studies. Moreover, all previous theoretical calculations have focused mainly on bulk magnetism. Thus it would be interesting to analyze the occurrence of phase separation and/or defect creation within a first principles study. Experimentally, we have seen that K$^+$/Ti$^{4+}$ substitution is not thermodynamically possible due to the large difference between charge or/and radius size. However, the introduction of K into TiO$_2$ induces some magnetism but the magnetic moment is far less than theoretically predicted and, in particular, there is no long-range ferromagnetic ordering.

To conclude, we have prepared TiO$_2$-K compounds by the solid state route. XRD, microstructural analyses with SEM, and XPS experiments provide the evidence that Ti$_{1-x}$K$_x$O$_2$ is thermodynamically unstable, and the hypothesis on which first principles calculations were based (substitution of K$^+$ in Ti$^{4+}$O$_2$ leading to ferromagnetism) is not realistic. Experimentally, weak but clear paramagnetic behavior (effective paramagnetic moment of $\sim 0.5 \mu_B$ K$^{-1}$ and no long-range ferromagnetic order) is observed when K ions are introduced in TiO$_2$. The difference in the nature of substitution explains the lack of ferromagnetic order and why this moment is much smaller than the predicted one of 3 $\mu_B$. One of the messages of this paper is that first principle calculations should be preceded by thermodynamical calculations evaluating the evolution of the most probable crystal structures after non-magnetic impurities are introduced.

References


Table 1. Parameters obtained from modified Curie–Weiss fitting. The effective paramagnetic moment, $\mu_{\text{eff}}$, was determined from the fitted Curie constant $C(x)$ by using the relation $\mu_{\text{eff}} = \sqrt{3k_B/C(N\mu_0\mu_B^2)}$ with $C(x) = xC_0$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$x_0$ ($10^{-5}$ emu/mol Oe)</th>
<th>$C$ ($10^{-4}$ K$^{-1}$ emu/mol Oe)</th>
<th>$\mu_{\text{eff}}$ ($\mu_B$)</th>
<th>$\mu_{\text{eff}}$ ($\mu_B/K$)</th>
<th>$\theta_p$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>0.79</td>
<td>1.40</td>
<td>0.033</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>K02</td>
<td>3.47</td>
<td>6.45</td>
<td>0.072</td>
<td>0.509</td>
<td>−1.22</td>
</tr>
<tr>
<td>K04</td>
<td>4.36</td>
<td>2.43</td>
<td>0.044</td>
<td>0.220</td>
<td>1.39</td>
</tr>
<tr>
<td>K06</td>
<td>5.06</td>
<td>5.70</td>
<td>0.068</td>
<td>0.282</td>
<td>−1.79</td>
</tr>
</tbody>
</table>

Figure 5. (a) Temperature variation of $\chi T$ and (b) temperature variation of modified inverse susceptibility and the corresponding Curie–Weiss fitting. The inset shows the fitting for TiO$_2$.  

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