

Multiferroicity in V-doped PbTiO₃

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Abstract. We report *ab initio* predictions on the proper multiferroic (ferromagnetic, insulating and ferroelectric) character of PbTiO₃ doped with vanadium (V). Ferromagnetically coupled V impurities carry a magnetization of 1 μ_B each. The coupling is expected to be strong, since the paramagnetic solution is higher by 150 meV/vanadium, and no stable antiferromagnetic solution was found. The electronic gap in the doped system is about 0.2-0.3 eV in the generalized gradient approximation (GGA), hence the system is properly multiferroic. V doping increases the spontaneous polarization in PbTiO₃, with an approximate percentual rate of 0.7 $\mu C/cm^2$.

1. Introduction

Modern technology uses extensively ferroic materials –i.e. having a spontaneous and permanent order parameter of one kind or another– with fairly exotic properties. For example, commodity data-storage devices exploit ferromagnets with giant magnetoresistance in magnetic random-access memories, in a continued push toward increased information density and reduced dimensions and writing energy. Besides their traditional use in sensors and actuators, ferroelectrics –with their permanent and switchable electrical polarization– are the building block of non-volatile, high speed, random-access memories which promise performances superior to semiconductor flash memories.

While their existence has been known since the 1960s, multiferroics, i.e. materials where polarization P and magnetization M coexist [1, 2], have enjoyed a renaissance in recent years, because of great improvements in growth techniques and new theoretical approaches. The coexistence of several order parameters and their mutual coupling may open the way to new device concepts, including the electrical addressing of magnetic memories without magnetic fields and their generating currents; the creation of multi-layer multi-state logical devices, exploiting combinations of polarization and magnetization; and magnetoelectric sensors. However, most of the current multiferroics lack sufficiently strong polarization or magnetization, or sufficient magnetoelectric coupling, or the correct kind of magnetic order (ferromagnets are desired, but antiferromagnets are much more common).

Some of the difficulties of single-phase multiferroics are bypassed by “metamultiferroics” built of multilayer heterostructures of ferromagnets and ferroelectrics [3], as for example in multiferroic tunnel junctions (MFTJ), where ferromagnetic electrodes are separated by a ferroelectric insulating barrier. The resistance against tunneling across the junction depends on the relative orientation of magnetization of the two electrodes (magnetoresistance) and on the direction of ferroelectric polarization of the insulating layer (electroresistance). This enables in principle a



4-level switchable resistance using external electric and magnetic fields. Of course, a further magnetic degree of freedom in the insulating-barrier material could potentially duplicate the number of states, and any chance of locally tuning the magnetization would add further design leeway. Following this line of thought, in this paper we report an *ab initio* investigation strongly suggesting that PbTiO₃ (PTO) doped with V (V:PTO) is a ferromagnetic small-gap insulator, hence a proper multiferroic. This is particularly interesting in view of the giant electroresistance effect predicted in tunnel junctions with PTO as ferroelectric tunnel layer [4].

2. V doping of PTO

Here we report the first principles prediction of a multiferroic state of lead titanate doped with magnetic vanadium. PTO is a well-known tetragonal perovskite with a high spontaneous polarization ($86 \mu\text{C}/\text{cm}^2$) of displacive origin. PbVO₃ also happens to be tetragonal, and with an even higher spontaneous polarization ($152 \mu\text{C}/\text{cm}^2$). Previous studies have shown its ground state to be an antiferromagnetic insulator (C-type), making it not especially interesting as a multiferroic. Motivated by our previous study of V-doped ferroelectric titanates [5], we examine the magnetic properties of vanadium diluted within the robust PTO ferroelectric.

Ab initio calculations are performed within density functional theory in the generalized gradient approximation (GGA) by Perdew-Wang using the PAW method [6, 7] as implemented in the VASP code [8]. Standard cutoff is used for the plane wave basis, and the k-point mesh for the bulk is $8 \times 8 \times 8$ (appropriately rescaled for defect super cells). The Berry phase technique is used to calculate the polarization change upon V doping, using strings of 16 points in the polarization direction.

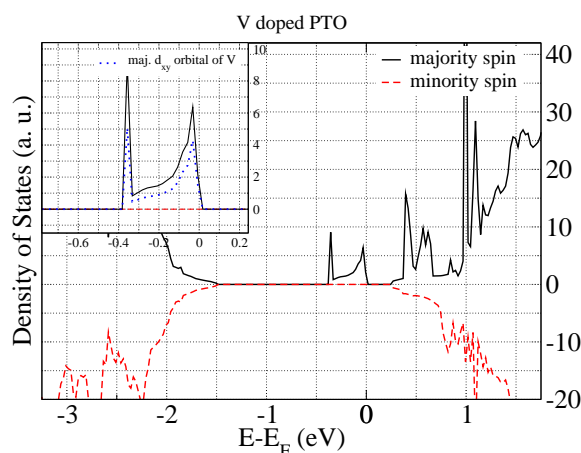


Figure 1. Density of states for V:PTO. Positive curve is majority spin, negative is minority spin. Fermi energy is at 0 eV. Inset shows a zoom of the gap peak. The dotted line is a V *d*-up.

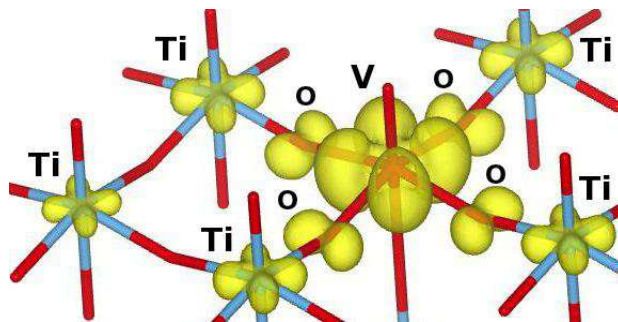
After studying PTO and PVO in the respective ferroelectric phases, we substituted V for one Ti in a $2 \times 2 \times 2$ tetragonal supercell of ferroelectric PTO, i.e. dopant concentration $\sim 12.5\%$. A selection of structure parameters (lattice constants, distance of V or Ti from neighbouring O along the polar axis) are collected in table 1. V has one excess electron compared to Ti, so it is, as expected, spin-polarized with a moment of $1 \mu_B$. Orbital angular momentum is assumed to be quenched. Figure 1 displays the key result, i.e. the density of states (DOS) of ferromagnetic V:PTO. As we can observe, a fully occupied peak appears in the gap of PTO, placed so that a gap of about 0.2 eV survives. This DOS feature is obviously related to the excess V electron occupying antibonding conduction states. Indeed, as shown in the inset, the main contribution to that peak is that of spin-up *d* orbitals of V. Thus, PTO doped with vanadium is a small-gap

Table 1. Cell parameters for V doped PTO, bulk PTO and PVO. Theoretical values are calculated for this work in GGA approximation. Experimental values are from references [9, 10]

	V:PTO	PTO (Theor. / Expt.)	PVO (Theor. / Expt.)
a	7.848	3.924 / 3.895	3.806 / 3.804
c	8.351	4.175 / 4.171	4.979 / 4.677
V-O _{top}	1.709	-	1.700 / 1.677
V-O _{down}	2.377	-	3.278 / 3.01
Ti-O _{top}	1.792	1.795 / 1.75	-
Ti-O _{down}	2.380	2.380 / 2.42	-

ferromagnetic insulator thanks to the unpaired electron of dopant vanadium. The gap of PTO is of course underestimated due to the known gap error of semi-local functionals [12]; it may well be that the small V-related gap is also somewhat larger than calculated due to the same effects (self-interaction, xc discontinuity, etc.).

In the cell just discussed, V is ferromagnetic by construction, being coupled to its periodic images. To study an antiferromagnetic configuration we consider two V's at the same concentration in a $2\sqrt{2} \times 2\sqrt{2} \times 2$ tetragonal cell. The two V are placed in that cell as far as possible from each other. While the ferromagnetic configuration is stable, the antiferromagnetic configuration is not. The V moments disappear and the system converges to a metallic Pauli paramagnet of zero moment, which is about 300 meV higher in energy than the ferromagnet. Of course, this prevents the evaluation of a coupling parameter for magnetic models, but the ferromagnet seems quite stable nevertheless.

**Figure 2.** Majority spin density of the spin-polarized electron of V in the basal plane (iso-level: $10^{-3} e/\text{\AA}^3$). The state is anti-bonding with first-neighbor O's, has d_{xy} -like nodal structure, and propagates through d_{xy} -like Ti states. Charge paths along the vertical axis are negligible.

Inspection of the charge density of the impurity state (Fig. 2) suggests a d_{xy} -like nodal structure and coupling of V's via V-O-Ti-O... paths in the basal plane, whereas hardly any density is to be found along the vertical axis. While the V-centered state is, as expected, anti-bonding with first neighbors, the bonding O-V states (which mimic those of the substituted Ti) appear to make for a larger charge accumulation in the V-O bond region (Fig. 3), matching the shorter V-O bond length compared to Ti-O (1.71 vs 1.79 Å).

Following Ref.[11], the equilibrium concentration is $[V]=N_s \exp(-E_f(V)/kT_g)$, where N_s is the density of Ti sites and T_g the growth temperature. Assuming that the solubility limit for V in PTO is PVO, i.e. that high V contents will eventually cause phase separation of PVO, the formation energy is $E_f(V)=E(\text{V:PTO})-(n-1)E(\text{PTO})-E(\text{PVO}) \approx 1.23$ eV, involving the total

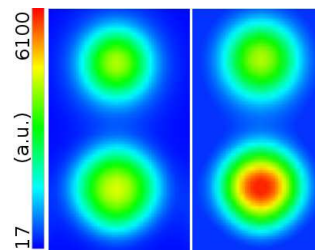


Figure 3. Total charge density (in arbitrary units) in the vertical plane across a Ti-O bond in PTO (left) and a V-O bond in V:PTO. A slightly larger bond charge can be appreciated in V:PTO.

energy of the doped supercell of V:PTO comprising n unit cells, and of the unit cells of PTO and PVO. Since $N_s = 1.25 \cdot 10^{23} \text{cm}^{-3}$, at a typical $T_g = 650$ K we find a logarithmic concentration $\log_{10} [V] \approx 13.4$, which may increase perhaps to about 16 due to vibrational entropy (V is heavier than Ti). This thermodynamic solubility limit is relatively low, but it may well not apply whenever kinetics or non-equilibrium phenomena become dominant, as it happens in modern epitaxial growth techniques.

Finally, we estimated the changes in polarization induced by V doping. At 12.5% V we find a polarization increase of $8.3 \mu\text{C}/\text{cm}^2$, which agrees nicely with $8.25 \mu\text{C}/\text{cm}^2$ obtained by linear interpolation between the bulk values of PTO and PVO mentioned previously. Therefore, in terms of polarization, V does not seem detrimental, but in fact benign.

3. Conclusions

In summary, we presented an *ab initio* prediction of the proper multiferroicity of V-doped PTO. The gap is about 0.2-0.3 eV and the magnetization is $1 \mu_B/\text{V}$, or 1.5×10^{22} spins/ cm^3 at our chosen V density. We predict the polarization to increase linearly with V concentration at the percentual rate of $0.7 \mu\text{C}/\text{cm}^2$. Presumably this will only apply at relatively low concentrations, since the antiferromagnetic character of PVO will eventually take over.

Note – During review we have become aware of a very recent study [13] of transition-metal doping in a perovskite ferroelectric (BaTiO_3), reporting results in general agreement with the ones just presented.

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