Magnetic instability induced giant magnetoelectric coupling

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Materials with coupled responses to external electric and magnetic fields present entirely new design opportunities for multifunctional, miniaturized devices such as memory elements, sensors and actuators, aside from their high fundamental importance. Such ‘multiferroic’ or ‘magnetoelectric’ materials attract a lot of research attention. Magnetoelectric materials possess spontaneous magnetic ordering by cooperative arrangements of magnetic moments as well as spontaneous electric polarization arising from coherent arrangement of electric dipoles. Such magnetism and ferroelectricity very seldom coexist and even if they do coexist, the interplay between them is usually too weak to find real applications in devices with multifunctionalities. By means of density functional calculations, we here demonstrate a giant magnetoelectric coupling in BiCoO$_3$, originating from a magnetic instability/metamagnetism facilitated by a spin-state transition of cobalt. Giant ferroelectric polarization is found to accompany the metamagnetic transition due to an unusually large difference in equilibrium structural parameters of the paraelectric (low spin-state) and the ferroelectric (high spin-state) phases. Our results suggest that a giant coupling between electric and magnetic degrees of freedom can be obtained for multiferroic materials when they are on the verge of metamagnetic transitions and in extreme cases one can change the material from magnetic to nonmagnetic (and vice versa) by switching the electric field, thus progressing to novel device applications.

Understanding the coupling between magnetism and ferroelectricity is of high fundamental and technological importance.[1-5] E.g., a sufficiently strong coupling between magnetic and dielectric properties may enable switching of the magnetization by means of an electric field, thereby reducing the thermal power needed for a magnetic memory drastically. If electric writing and magnetic reading were to be used, one of the layers in spin valves composed of ferromagnetic and magnetoelectric layers, would no longer have to be pinned.[6] Giant magnetoelectric materials facilitate highly efficient elastic interactions and a strong magnetic response to an electric field (or vice versa) via magnetostriction and piezoelectric effects.[7, 8] Several materials possess both
ferroelectricity and cooperative magnetism; however, the coupling between these properties is not necessarily large. The structural and electronic circumstances that would favour a large coupling remain unexplored, partly due to the lack of materials with a large coupling. Here we report that such a large coupling occurs in BiCoO$_3$, for which an external electric field can induce a strong magnetic response by changing the spin-state of cobalt from a magnetic high spin (HS) state to a nonmagnetic low spin (LS) state.

The simultaneous presence of strong electron-electron interaction within the transition metal $d$ manifold and a sizable hopping-interaction strength between the transition metal $d$ and oxygen $p$ states are primarily responsible for a wide range of properties exhibited by perovskite-like oxides. Several ferroelectric perovskites undergo a phase transition from a high-temperature, high-symmetry phase that behaves as an ordinary dielectric, to the spontaneously polarized phase at low temperature. Considerable research activities are focused on understanding the nature of and the driving force for such ferroelectric transitions. The electric and magnetic properties of cobaltites depend on the spin-state of the Co ions, i.e., whether they are in LS, intermediate spin (IS) or HS states (simplified pure ionic limit). For example, LaCoO$_3$ is a diamagnetic insulator at low temperature and transforms to the paramagnetic state at 90K due to an LS-IS transition.$^{[9, 10]}$ Metamagnetism from spin-state transitions may give rise to exciting phenomena such as giant magnetoresistance,$^{[11]}$ giant magnetocaloric effect,$^{[12]}$ shape memory effect,$^{[13]}$ etc. We show presently that metamagnetism can also lead to giant magnetoelectric coupling. Generally, spin-state transitions are induced by hole/electron doping, temperature, magnetic field, pressure, and/or lattice strain. For the first time we here show that spin-state transitions can also be induced by an electric field in the case of magnetoelectric materials which display magnetic instabilities.

Materials with pure ionic bonding typically possess centrosymmetric structures owing to the minimizing of short-range Coulomb repulsions and they are hence nonferroelectric. The noncentrosymmetry required by a ferroelectric material is therefore determined by a balance between the above mentioned Coulomb forces and additional electronic aspects such as covalency, presence of non-bonded electrons (lone pairs) etc. A common mechanism for ferroelectricity is displacement of an empty $d$-shell transition metal ion owing to strong covalent bonding with neighbouring ligands.$^{[14]}$ On the other hand, one needs atoms with unpaired ($d$-shell) electrons in order to achieve cooperative magnetism. Thus at first sight magnetism and ferroelectricity may seem to be mutually exclusive.$^{[5, 15]}$ However, several other mechanisms may also provide magnetoelectric behaviour, e.g. lone pairs in the nonmagnetic cations such as Bi in BiMnO$_3$.$^{[16]}$
magnetic frustration in TbMnO$_3$,[1] electrostatic and size effects in YMnO$_3$ where long range dipole-dipole interactions and oxygen rotation drive ferroelectricity,[17], and charge- and orbital-ordered systems where the coupling between magnetic and charge ordering creates magneto-electricity.[18]

We have found by using state-of-the-art DFT-calculations (see Methodology section) that the perovskite-like oxide BiCoO$_3$ with C-type antiferromagnetic (C-AF) ordering (see Fig.1) exhibits giant magneto-electric coupling as well as giant ferroelectric polarization. Of particular importance is a metamagnetic transition induced by a small compression or by an electric field. This extraordinary coupling with giant polarization is demonstrated by: (1) a much larger value for the calculated spontaneous ferroelectric polarization for BiCoO$_3$ than for e.g. the isostructural magnetoelectrics PbVO$_3$ and BiFeO$_3$; (2) a pressure-induced metamagnetic transition, where BiCoO$_3$ transforms from the HS state to a nonmagnetic LS state with ~5% volume compression (see Fig.2). The calculated equilibrium volume for the paraelectric phase is found to be that of LS phase. Likewise, the calculated density of states shows that the Co in paraelectric phase resembles nonmagnetic LS state and that in ferroelectric phase show magnetic HS state (see Fig. 4). The observed giant magneto-electric effect and magnetic instability are unique in this material and as a result it has the largest ferroelectric polarization among magnetoelectric materials identified so far.

Very limited experimental knowledge exists for the magneto-electric behaviour of BiCoO$_3$ owing to difficulties in preparing high quality samples. The Néel temperature for ferroelectric BiCoO$_3$ is 470 K according to magnetic susceptibility measurements.[19] Our calculations show that the magnetic ground state for the ferroelectric phase of BiCoO$_3$ will be C-AF. The calculated total energy for the ferroelectric phase in the ferromagnetic, A-type and G-type antiferromagnetic states are found to be respectively 268, 120 and 28 meV/f.u. higher than for the C-AF phase. The present observation of C-AF magnetic ordering for ferroelectric BiCoO$_3$ is in agreement with low temperature neutron diffraction data.[19] The calculated total spin-only moment for the C-AF phase is 2.90 $\mu_B$/f.u. while the orbital moment at the Co site obtained from orbital polarization calculation is 0.20 $\mu_B$/Co. The calculated total moment of 3.10 $\mu_B$/f.u. is comparable with 3.24$\mu_B$ measured from neutron diffraction measurements at 5K. Interestingly 2.74 $\mu_B$ of the spin moment resides at the Co site, the rest at the oxygen sites owing to covalent magnetism. For the paraelectric phase our total energy calculations predicted that the nonmagnetic solution is the ground state (see Fig.3 and 4).
In order to study the ferroelectric behaviour we calculated the Born effective charges (BEC) using the Berry phase approach \[20, 21\] generalized to spin-polarized systems. BEC \((Z^*)\) is defined as a linear term in the polarization change due to a unit displacement of an ion, keeping all other ions fixed under the condition of zero macroscopic field. A large \(Z^*\) indicates that the force acting on a given ion due to the electric field generated by the atomic displacements is large even if the field is small, thus favouring a polarized ground state. The calculated average diagonal components of \(Z^*\) values are \(Z^*_{\text{Bi}} = 4.3\), \(Z^*_{\text{Co}} = 1.8\), \(Z^*_{\text{O(apex)}} = -2.20\), and \(Z^*_{\text{O(base)}} = -1.94\). Note that there are two kinds of oxygen atoms in the crystal structure of \(\text{BiCoO}_3\), one at the apical (Co-O\text{apex} distance 1.774 Å) and four at the base (Co-O\text{base} distance 1.995 Å) of the CoO\text{5}-square pyramid (see Fig.1).

The tetragonality of \(\text{BiCoO}_3\) is much larger \((c/a = 1.28)\) than that of the well known ferroelectric \(\text{PbTiO}_3\) \((c/a = 1.06;\) polarization = 81 \(\mu\text{C/cm}^2\))^\[14\]. Hence, one expects a giant polarization in \(\text{BiCoO}_3\). The total polarization for \(\text{BiCoO}_3\) from the present Berry phase calculation is 170 \(\mu\text{C/cm}^2\), in good agreement with 179 \(\mu\text{C/cm}^2\) reported earlier.\[22\] The similarly calculated total polarization for the isostructural compounds \(\text{BiFeO}_3\) and \(\text{PbVO}_3\) are 158 and 138 \(\mu\text{C/cm}^2\), respectively. These predicted giant polarization values are in good agreement with the value of 150 \(\mu\text{C/cm}^2\) observed experimentally for thin films of \(\text{BiFeO}_3\) \[23\] and 152 \(\mu\text{C/cm}^2\) for \(\text{PbVO}_3\) obtained from earlier Berry phase calculation.\[22\] The calculated polarization for \(\text{BiCoO}_3\) is the largest among the magnetoelectric materials identified so far. The partial polarization analyses show that the net polarization is mainly originating from displacements of the oxygen atoms with respect to the centrosymmetric structure and they are particularly large along the \(c\)-axis of the crystal structure. Although the displacement with reference to the centrosymmetric structure is smaller for \(\text{O}_{\text{apex}}\) than that for \(\text{O}_{\text{base}}\), their polarization contributions are comparable. This occurs owing to the larger value of the \(zz\) component of BEC at the apical site \((Z^*_{\text{O(apex)}} = -2.65, Z^*_{\text{O(base)}} = -1.83)\) caused by shorter bond length from covalency effects. The volume change corresponding to the paraelectric-ferroelectric transition is very large \((17\%;\) see Fig. 3) unlike in other ferroelectric materials with lone-pair electrons. This is due to a huge magneto-volume effect, arising from the spin-state transition. The increased polarization in \(\text{BiCoO}_3\) compared with \(\text{BiFeO}_3\) and \(\text{PbVO}_3\) is mainly due to the larger displacements of the oxygen atoms from the centrosymmetric structure and this is associated with changes in the Co–O bond length between the ferroelectric and paraelectric phases owing to metamagnetism.

The presence of lone-pair electrons at the Bi site (seen from electron-localization-function plot) and orbital projected DOS (see Fig.4) indicate that the formal valence for Co ions can be assigned as 3+.
and we made the following analysis accordingly. In an ideal square-pyramidal crystal field the $d$ levels will split into nondegenerate $b_{2g}$ ($d_{xy}$), doubly degenerate $e_g$ ($d_{xz}$, $d_{yz}$), nondegenerate $a_{1g}$ ($d_{z^2}$), and $b_{1g}$ ($d_{x^2-y^2}$) levels. In pure ionic picture Co$^{3+}$ with six $d$ electrons will fill these energy levels either with a LS state ($b_{2g}^2$ $e_g^4$ $a_{1g}^0$ $b_{1g}^0$) or with a HS state ($b_{2g}^2$ $e_g^2$ $a_{1g}^1$ $b_{1g}^1$) having spin moments 0 and 4 $\mu_B$, respectively. Accordingly our orbital projected DOS in Fig.4 for the paraelectric and ferroelectric phases show LS and HS state for Co, respectively. Usually the calculated magnetic moments are smaller than that for the pure ionic case owing to covalence effects. Hence, the calculated moment of 3.10 $\mu_B$ in the ferroelectric phase may be interpreted as that for Co in HS state. The variation in total energy as a function of magnetic moment is shown for different unit cell volumes of BiCoO$_3$ in Fig.2 as obtained from fixed spin calculations. The curves show that the energy difference between the LS and HS state is $\approx$0.1 eV/f.u. and for a 2.5% volume compression the LS and HS states becomes almost energetically degenerate. Around 5% volume compression the LS state is found to be lower in energy than the HS state. This indicates the presence of metamagnetism in the system. In support to our detection of metamagnetism in BiCoO$_3$, an experimental study shows that the heating and cooling magnetization curves do not coincide if the sample has been heated above 600K.[19]

We have shown that strong magneto-electric coupling can be achieved in materials having a magnetic instability. This finding opens up new possibility to find potential materials where one can vary the magnetic properties drastically (in extreme cases from a magnetic state to a nonmagnetic state, and vice versa as shown here) by means of an electric field. Such strong coupling of magnetic and electric order parameters has possibilities for applications in spintronic devices. One may envisage data-storage media being alternatives to magneto-optical disks where the slow magnetic writing process is replaced by a fast magnetization reversal through the use of electric fields. Thus we have described a new route to giant magnetoelectricity, which is strongly interwoven with an associated magnetic instability. This exciting concept will stimulate further research towards designing novel multiferroics for practical applications.

**Methodology:**

The present investigation is based on *ab initio* electronic structure calculations derived from spin-polarized density functional theory (DFT). First principles DFT calculations were performed using the Vienna *ab initio* simulation package (VASP) [24] within the projector augmented wave method. In order to identify the magnetic ground state we have considered the nonmagnetic, ferromagnetic, $A$-type antiferromagnetic ($A$-AF; where the intraplane exchange interaction is ferromagnetic and
interplane interaction is antiferromagnetic), $C$-type antiferromagnetic ($C$-AF; where the intraplane exchange interaction is antiferromagnetic and interplane interaction is ferromagnetic), and $G$-type antiferromagnetic ($G$-AF; where both intraplane and interplane exchange interactions are antiferromagnetic). \[25\] We have used very large basis set with 875 eV for the plane-wave cut-off in order to reproduce the structural parameters and polarization values correctly. \[26\] Conventional spin-polarized calculations based on DFT allows the moment to float and the ground state is obtained by minimizing the energy functional with respect to the charge and magnetization densities under the constraint of a fixed number of electrons. In order to study metamagnetism it is advantageous to calculate the total energy as a function of magnetic moment using the so-called fixed-spin-moment method, \[27\] where one uses the magnetic moment $M$ as an external parameter and calculates the total energy as a function of $M$. The BEC are calculated using the so called “Berry phase finite difference approach” in which the electronic contribution to the change of polarization is estimated using modern theory of polarization. \[20,21\] The orbital moment was calculated using the orbital polarization correction method implemented in the Wien2k package. \[28\]
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Fig.1 Magnetic structure of BiCoO$_3$ doubled along $c$-axis, where the arrows at the Co atoms indicate the C-type spin ordering. The square-pyramidal environment of Co atoms is indicated by polyhedra. The magnetic structure is found to be a tetragonal structure (space group $P4mm$) with lattice parameters $a = 7.4608$ (7.4398), and $c = 4.7897$ (4.7196) Å and the positions of the atoms are Bi 4d [0.75 0.25 0.0], Co1 2c [0 0.5 0.4282(0.4336)], Co2 1b [0.5 0.5 0.4282(0.4336)], Co3 1a [0 0 0.4282 (0.4336)], O1 2c [0.5 0.7985 (0.7976)], O2 1b [0.5 0.5 0.7985 (0.7976)], O3 1a [0 0 0.7985(0.7976)], O4 4e [0.75 0.0 0.2806(0.2689)], and O5 4f [0.75 0.5 0.2806 (0.2689)] respectively, where the values in the bracket are derived from the experimental neutron diffraction measurements at 5 K.
Fig. 2 Variation of total energy with magnetic moment for BiCoO$_3$ obtained from the fixed-spin calculation for different volumes. The total energy for the nonspin-polarized case is set to zero. Note that for the equilibrium volume and 2.5% volume compression the high-spin state with moment around ~3.6 $\mu_B$ is found to be lower in energy, and for further volume compression, the low-spin state becomes stable.
Fig. 3 Calculated total energy versus volume curves for C-AF ferroelectric and paraelectric phases of BiCoO$_3$. The discontinuity in the total energy curve for the ferroelectric phase is associated with the metamagnetic transition from the HS state at the equilibrium volume to the LS state. It should be noted that the equilibrium volume for the paraelectric phase is closer to the volume corresponding to the local minimum in the ferroelectric phase. The large change in equilibrium structural parameters associated with the magnetic instability results in giant magnetoelectric effect. The inset shows variation of magnetic moment at the Co site with volume in the C-AF BiCoO$_3$. 
Fig. 4 Calculated orbital-projected density of states for BiCoO$_3$ in the (a) ferroelectric and (b) paraelectric phases.

Keywords: metamagnetism, magnetoelectrics, spin-state transitions, magnetoelectric coupling, magnetic structure.