Lock-in spin structures and ferrimagnetism in polar Ni$_{2-x}$Co$_x$ScSbO$_6$ oxides

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The new phase Co$_2$ScSbO$_6$ and Ni$_2$Co$_x$ScSbO$_6$ solid solutions adopt the polar Ni$_2$TeO$_4$-type structure and order magnetically below 60 K. A series of long period lock-in [0 0 1/3n] spin structures with $n = 5, 6, 8$ and 10 is discovered, coexisting with a ferrimagnetic [0 0 0] phase at high Co-contents. The presence of electrical polarisation and spontaneous magnetisations offers possibilities for multiferroic properties.

Multiferroics combining magnetic and ferroelectric orders have been intensively investigated for a range of potential applications. Materials showing magnetically induced ferroelectricity often have strong magnetoelastic couplings at low temperatures, and geometrically frustrated spin networks favour large magnetoelastic effects, as the development of non-collinear spiral magnetic structures can break the inversion symmetry and consequently allow a net polarization. Cation-ordered structures based on the corundum type have been of great interest for multiferroic properties as the LiNbO$_3$, Ni$_3$TeO$_4$, and ilmenite types are all polar permitting ferroelectricity. Frustrated honeycomb layers of transition metal cations can lead to helical spin structures that may give rise to magnetically induced ferroelectricity, for example, in the Mn$_2$B$_2$O$_6$ family.

The Ni$_2$TeO$_4$ (NTO, space group R3) type Ni$_2$ScSbO$_6$ has been reported to be ferroelectric below 1050 K and to have a helimagnetic structure with propagation vector $\mathbf{k} = [0 0.036 0]$. The presence of four crystallographically independent cation sites in the NTO-type structure provides chemical degrees of freedom to manipulate the physical properties. Here we report a new analogue Co$_2$ScSbO$_6$ and the complex evolution of magnetic orders across the Ni$_2$Co$_x$ScSbO$_6$ series.

The net ferroelectric polarization of $P_z = 19.91 \mu$C/cm$^2$ calculated from a point charge model is comparable to the value for Ni$_2$ScSbO$_6$ of $P_z = 13.27 \mu$C/cm$^2$. Rietveld fits to 100 K NPD data of the $x = 0, 0.5, 1$ and 1.5 samples confirm that a continuous NTO structure coexists with the Ni$_2$ScSbO$_6$ as inset in Fig. 1. However, structure refinement revealed 21% substitution of Sc by Co, resulting in a Sc-deficient overall composition Co$_{2-x}$Sc$_x$Co$_{2-x}$Sb$_6$O$_{18}$. The net ferroelectric polarization of $P_z = 19.91 \mu$C/cm$^2$ calculated from a point charge model is comparable to the value for Ni$_2$ScSbO$_6$ of $P_z = 13.27 \mu$C/cm$^2$. Rietveld fits to 100 K NPD data of the $x = 0, 0.5, 1$ and 1.5 Ni$_2$Co$_{2-x}$ScSbO$_6$ samples confirm that a continuous NTO-type solid solution is formed with lattice parameters increasing with $x$. No Sc/Ni disorder is observed in Ni$_2$ScSbO$_6$, in agreement with a...
previous study, but a substitution of Sc by Co that increases with \(x\) is observed across the series as shown in the inset of Figure 1. Refinement procedures, fits and results are explained and shown in ESI.

ZFC magnetic susceptibility measurements and magnetization-field loops at 2 K are shown in Fig. 2. Co\(_2\)ScSb\(_6\) is ferrimagnetic below \(T_C \approx 60\) K, with a spontaneous moment of 0.2 \(\mu_B/\text{formula unit}\) at 2 K. A Curie-Weiss fit to the high temperature reciprocal susceptibility gives a Weiss constant of \(-142\) K suggesting dominant antiferromagnetic interactions between spins and the effective paramagnetic moment of \(\mu_{\text{eff}} = 7.61 \mu_B/\text{f.u.}\) is equivalent to 5.38 \(\mu_B\) per high spin Co\(^{2+}\). Similar values \(\approx 5.20 \mu_B\) have been reported for other Co\(^{2+}\) oxides with a strong \(^{4}\text{Ti}\) excited state orbital contribution to the moment.\(^{18-19}\)

The other Ni\(_{2+x}\)Co\(_2\)ScSb\(_6\) compositions also have magnetic transitions near 60 K. Curie-Weiss fitting results, summarized in Table 1, show that all of the effective magnetic moments are close to calculated values for the corresponding proportions of spin only Ni\(^{2+}\) (\(\mu_{\text{eff}} = 2.83 \mu_B\)) and Co\(^{2+}\) (\(\mu_{\text{eff}} = 5.20 \mu_B\) is assumed). \(M-H\) loops show a change in the bulk magnetic properties as Co is introduced. \(x = 0\) Ni\(_2\)ScSb\(_6\) is antiferromagnetic with linear \(M-H\) but \(x = 1\) and 1.5 samples have a similar ferrimagnetic behaviour to Co\(_2\)ScSb\(_6\), with spontaneous magnetizations extrapolated to zero field of \(M_0 \approx 0.2 \mu_B\) at 2K. \(x = 0.5\) shows metamagnetism with a critical field of 1.5 T at 4 K, and metamagnetic transitions are also observed for \(x = 0.5\) and 1 samples at 40 K as shown in ESI. The observation of spontaneous magnetizations for the Co-rich materials in this polar NTO-type family demonstrates potential for multiferroism.

Table 1. Magnetic parameters for Ni\(_{2+x}\)Co\(_2\)ScSb\(_6\) materials; \(T_C\), Weiss constant \((\theta)\), effective moments \((\mu_{\text{eff}})\), critical field \((H_C)\) and spontaneous magnetization at 2 K \((M_0)\) determined from magnetic measurements (top); ordered moment \((\mu)\), refined propagation vector component \((k = k_x, k_y, k_z)\) for \(x = 0, 1\) \((k = k_x, k_y, k_z \neq 0)\), \(1/3n\) periodicity for integer \(n\), and % of the \([00k]\) magnetic phase coexisting with \([000]\) for \(x = 1.5\) and 2 (bottom).

| \(x\) | 0 | 0.5 | 1 | 1.5 | 2 |
|-------|---|-----|---|-----|---|
| \(T_C\) (K) | 65 | 61 | 59 | 58 | 59 |
| \(\theta\) (K) | -144 | -104 | -105 | -106 | -142 |
| \(\mu_{\text{eff}}\) (\(\mu_B\)) | 4.41 | 5.18 | 5.97 | 6.66 | 7.61 |
| \(\mu_{\text{eff}}\) (\(\mu_B\)) | 4.00 | 5.05 | 5.92 | 6.68 | 7.35 |
| \(H_C\) (T) | - | 1.5 | 0.7 | - | - |
| \(M_0\) (\(\mu_B/\text{f.u.}\)) | - | 0.15 | 0.2 | 0.22 | 0.14 |

| \(\mu\) (\(\mu_B\)) | 1.72(3) | 2.18(2) | 2.40(1) | 2.63(3) | 2.94(1) |
| \(\mu_{\text{eff}}\) (\(\mu_B\)) | 2.00 | 2.25 | 2.50 | 2.75 | 3.00 |
| \(k\) | 0.036(1) | 0.066(1) | 0.056(1) | 0.041(1) | 0.032(1) |
| \(1/3n\) | - | 0.067 | 0.056 | 0.042 | 0.033 |
| \(n\) | - | 5 | 6 | 8 | 10 |
| \%([00k]) | 100 | 100 | 84.8(1) | 63.4(1) |

Figure 3 shows the evolution of the principal magnetic diffraction contributions in the Ni\(_{2+x}\)Co\(_2\)ScSb\(_6\) series, obtained by subtracting the 100 K from the 4K NPD profiles (collected from WISH@ISIS for \(x = 2\); SPODI@FRMII for \(x \neq 2\)). \(x = 0\) Ni\(_2\)ScSb\(_6\) has prominent magnetic satellite reflections around the \((101)\) peak and a magnetic \((003)\) peak, which arise from an incommensurate \([0 k_0]\) magnetic propagation vector. As noted previously, NPD cannot distinguish between a helical model with spins confined to the \(xz\) plane and a cycloidal model with spins in the \(yz\) plane, and the latter is shown in Figure 4(a).

Introduction of Co\(^{2+}\) to give the \(x = 0.5\) sample leads to a dramatic change in the magnetic scattering as the splitting between \((101)\) satellites decreases greatly, and a new pair of satellites appears around \((003)\) while the fundamental peak disappears. These were indexed by a different \([0 0 k_z]\) propagation vector corresponding to a helical spin structure as shown in Fig. 4(b). The \([0 0 k_z]\) phase persists across all the Co-doped samples with a decrease in \(k_z\), as evidenced by the decreasing splitting between satellite pairs in Fig. 3. It is notable that all four measured \(k_z\) values are within error of \(1/3n\) periodicities for integers \(n = 5, 6, 8\) and 10. This demonstrates that the \([0 0 k_z]\) magnetic structures are not incommensurate, but...
are instead locked into a series of long period commensurate spirals (up to 420 Å for $n = 10$ Co$_3$ScSbO$_6$), as discussed later.

Fig. 3. Difference (4 K – 100 K) NPD patterns of Ni$_2$Co$_3$ScSbO$_6$ showing magnetic peaks. (003) and (101) peak positions are marked with dashed lines. Magnetic peaks from impurity Co$_{1.33}$ScO$_{0.64}$O$_4$ are identified with an asterisk.

Fig. 4. Magnetic structures of Ni$_2$Co$_3$ScSbO$_6$ for a) $x = 0$ with propagation vector $k = [0 k_1 0]$, b) $x = 0.5$ to 2 with $k = [0 0 k_2]$ and c) the competing commensurate $k = [0 0 0]$ phase for $x = 1.5$ and 2. Green and red arrows represent the Ni$^{2+}$/Co$^{2+}$ spins at M1 and M2 sites respectively.

Additional magnetic intensity at the (003) position arises for high Co-contents $x = 1.5$ and 2. This reveals an additional commensurate [0 0 0] magnetic phase with spin ordering as shown in Fig. 4(c). This corresponds to the $n \rightarrow \infty$ limit of the above [0 0 $k_1$] series. An important difference is that the [0 0 0] phase has antiparallel layers of inequivalent Co(Ni)1 and Co(Ni)2 site spins and so is ferrimagnetic, whereas these spin layers are successively rotated in the [0 0 $k_1$] spirals with finite $n$ which are thus antiferromagnetic. Results of magnetic refinements using the 4 K NPD data are summarised in Table 1.

The thermal evolution of the spin order for $x = 1.5$ has also been studied on instrument D20@ILL with wavelength $\lambda = 3.6$ Å and a take-off angle of 65°, providing a high resolution to resolve the satellite peaks from the fundamental magnetic reflections. Assuming the magnetic moments to have the same value in both [0 0 $k_1$] and [0 0 0] phases gives a saturation value of 2.94(1) $\mu_B$ for Co$_3$ScSbO$_6$ at 1.7 K, close to the ideal spin-only value of 3.00 $\mu_B$, and [0 0 $k_1$]:[0 0 0] phase proportions of 63 : 37. No changes to the magnetic order are found up to $T_C$ for any of the Ni$_2$Co$_3$ScSbO$_6$ materials. Furthermore, proportions of coexisting [0 0 $k_1$] and [0 0 0] phases for the $x = 1.5$ and 2 compositions also do not change, and the two phases appear to share a common $T_C$ as shown for Co$_3$ScSbO$_6$ in Fig. 5a, with further refinement results in ESI.

These results demonstrate a very rich magnetic behaviour in the Ni$_2$Co$_3$ScSbO$_6$ system as shown by the magnetic phase diagram derived from NPD and magnetisation measurements in Figure 5b. The strong magnetic anisotropy associated with orbitally-degenerate Co$^{2+}$ confines spins to the $xy$ plane for all Co-containing materials. This switches magnetic order from the incommensurate [0 $k_1$ 0] type previously reported for Ni$_2$ScSbO$_6$ to a new [0 0 $k_1$] helical antiferromagnetic arrangement for $x = 0.5$ to 2. This phase results from competition of antiferromagnetic couplings between nearest neighbour (NN) spin layers and next nearest neighbour (NNN) layers. NN couplings through Co/ Ni–O–Co/Ni bonds are strongly antiferromagnetic and NNN couplings through Co/ Ni–O–Sc/Sb– O–Co/Ni bridges are weaker and diminish relative to NN as $x$ increases resulting in a decrease in $k_1$.

Although the balance of NN and NNN couplings may favour incommensurate periodicities, the strong anisotropy of Co$^{2+}$ causes the spirals to lock into nearby commensurate values so that more spins can lie parallel to easy-axes which have a 3-fold symmetry in the $xy$ plane of the R3 crystal structure, hence the $1/3n$ values. $n = 5, 6, 8$ and 10 are observed at the $x = 0.5, 1, 1.5$ and 2 compositions respectively, and we speculate that other periodicities such as $n = 7$ and 9 may lie at intermediate compositions, as shown on the phase diagram. Studies of further Ni$_2$Co$_3$ScSbO$_6$ compositions will be needed to explore the full variety of spin structures. Lock-in orders are reported in other Co$^{3+}$ oxides such as CoCr$_2$O$_4^{20}$ and Co$_2$V$_2$O$_7^{22}$, but the Ni$_2$Co$_3$ScSbO$_6$ series represents an unusually rich series of lock-in phases accessible through chemical tuning at zero field strength.

The R3 lattice symmetry of the Ni$_2$Co$_3$ScSbO$_6$ materials allows linear or bilinear magnetoelectric effects, making these materials potential multiferroics. The electric polarisation, calculated to be in the range $E_0 = 13-20$ μC m$^{-2}$, is parallel to the z-axis. The observed net magnetisations of the Co-rich
samples probably arise from a combination of the presence of the ferrimagnetic [0 0 0] phase and spin canting within the [0 0 k] helical phases. The [0 0 0] phase has net magnetisation in the xy plane and so a perpendicular coupling mechanism between $M_0$ and $E_o$ may operate, as discussed for polar MnTiO$_3$. Canting of the spins in the [0 0 0] or [0 0 k] phases to give a small magnetization parallel to $E_o$ may also result from antisymmetric Dzyaloshinskii-Moriya coupling.

In conclusion, a new oxide Co$_2$ScSbO$_6$ has been synthesised at 6 GPa, and solid solutions Ni$_2$CoScSbO$_6$ ($x = 0 - 1.5$) were prepared at ambient pressure. All compositions adopt the Ni$_3$TeO$_2$-type structure with polar space group $R3$, and order magnetically below 60 K. A very rich magnetic phase diagram is discovered with magnetic order switching from an incommensurate [0 k 0] phase for pure Ni$_2$ScSbO$_6$ to a series of long-period lock-in [0 0 k] spin structures with $k_z = 1/3n$ for Co-containing $x = 0.5 - 2$ samples. These coexist with a ferrimagnetic [0 0 0] phase at $x = 1.5 - 2$. The presence of electrical polarisation and spontaneous magnetisations for Co-rich materials opens the possibilities for magnetoelectric coupling leading to multiferroic properties.

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Conflicts of interest
There are no conflicts of interest to declare.

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