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

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**The new phase  $\text{Co}_2\text{ScSbO}_6$  and  $\text{Ni}_{2-x}\text{Co}_x\text{ScSbO}_6$  solid solutions adopt the polar  $\text{Ni}_3\text{TeO}_6$ -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<sup>1</sup> combining magnetic and ferroelectric orders have been intensively investigated for a range of potential applications.<sup>2–3</sup> Materials showing magnetically induced ferroelectricity often have strong magnetoelectric couplings at low temperatures,<sup>4–5</sup> and geometrically frustrated spin networks<sup>6</sup> favour large magnetoelectric effects, as the development of non-collinear spiral magnetic structures can break the inversion symmetry and consequently allow a net polarization.<sup>7–8</sup> Cation-ordered structures based on the corundum type have been of great interest for multiferroic properties as the  $\text{LiNbO}_3$ ,<sup>9</sup>  $\text{Ni}_3\text{TeO}_6$ <sup>10</sup> and ordered ilmenite<sup>11</sup> 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  $\text{Mn}_2\text{BB}'\text{O}_6$  family.<sup>12</sup> The  $\text{Ni}_3\text{TeO}_6$  (NTO, space group R3) type  $\text{Ni}_2\text{ScSbO}_6$  has been reported to be ferroelectric below 1050 K and to have a helimagnetic structure with propagation vector  $k = [0\ 0.036\ 0]$ .<sup>13</sup> The presence of four crystallographically independent cation sites in the NTO-type structure provides chemical degrees of freedom to manipulate the physical properties.<sup>14</sup> Here we report a new analogue  $\text{Co}_2\text{ScSbO}_6$  and the complex evolution of magnetic orders across the  $\text{Ni}_{2-x}\text{Co}_x\text{ScSbO}_6$  series.

Polycrystalline specimens of  $\text{Ni}_{2-x}\text{Co}_x\text{ScSbO}_6$  ( $x = 0, 0.5, 1$  and  $1.5$ ) were synthesized by grinding together stoichiometric proportions of NiO, CoO,  $\text{Sc}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_5$  oxides under acetone, pelletizing the mixture, and heating between 973 K and 1373 K with intermediate grindings and temperature intervals of 100 K. However, attempts to make the  $x = 2$  composition by this method gave large amounts of the secondary  $\text{Co}_{2.33}\text{Sb}_{0.67}\text{O}_4$  spinel. A good quality sample of the new NTO-type material  $\text{Co}_2\text{ScSbO}_6$  ( $a = 5.225(1)$  Å,  $c = 14.017(1)$  Å) was prepared under high pressure and temperature conditions using a Walker-type multianvil apparatus. The precursor was pressed at 6 GPa, heated at 1273 K for 1 hour, slowly cooled and decompressed. Sample colours in the  $\text{Ni}_{2-x}\text{Co}_x\text{ScSbO}_6$  series gradually change from green to purple with increasing Co content and initial structural characterization using laboratory powder X-ray diffraction (XRD) showed that NTO-type phases are present throughout along with minor secondary phases ( $\text{Sc}_{5.5}\text{Sb}_{1.5}\text{O}_{12}$ ,  $(\text{Ni},\text{Co})\text{O}$  and  $\text{Co}_{2.33}\text{Sb}_{0.64}\text{O}_4$ ; proportions determined from Rietveld fits to NPD patterns are shown in ESI). High-resolution neutron powder diffraction (NPD) data have been collected on SPODI (FRMII, Munich), WISH (ISIS, Oxford) and D20 (ILL, Grenoble) diffractometers to determine cation distributions and precise oxygen positions (Ni, Co, Sc, Sb, and O neutron scattering lengths are respectively 10.30, 2.49, 12.29, 5.57 and 5.80 fm), and to determine low temperature magnetic structures for all the samples. Rietveld analysis was carried out using the Fullprof package<sup>15</sup> and Basireps<sup>16</sup> was used for magnetic structure analysis.

The Rietveld fit to 100 K NPD data (collected from WISH@ISIS) of  $\text{Co}_2\text{ScSbO}_6$  confirms that it adopts the NTO structure shown as inset in Fig. 1. However, structure refinement revealed 21% substitution of Sc by Co, resulting in a Sc-deficient overall composition  $\text{Co}_{2.16}\text{Sc}_{0.84}\text{SbO}_6$ . The net ferroelectric polarization of  $P_s = 19.91$   $\mu\text{C}/\text{cm}^2$  calculated from a point charge model<sup>17</sup> is comparable to the value for  $\text{Ni}_2\text{ScSbO}_6$  of  $P_s = 13.27$   $\mu\text{C}/\text{cm}^2$ . Rietveld fits to 100 K NPD data of the  $x = 0, 0.5, 1$  and  $1.5$   $\text{Ni}_{2-x}\text{Co}_x\text{ScSbO}_6$  samples confirm that a continuous NTO-type solid solution is formed with lattice parameters increasing with  $x$ . No Sc/Ni disorder is observed in  $\text{Ni}_2\text{ScSbO}_6$ , in agreement with a

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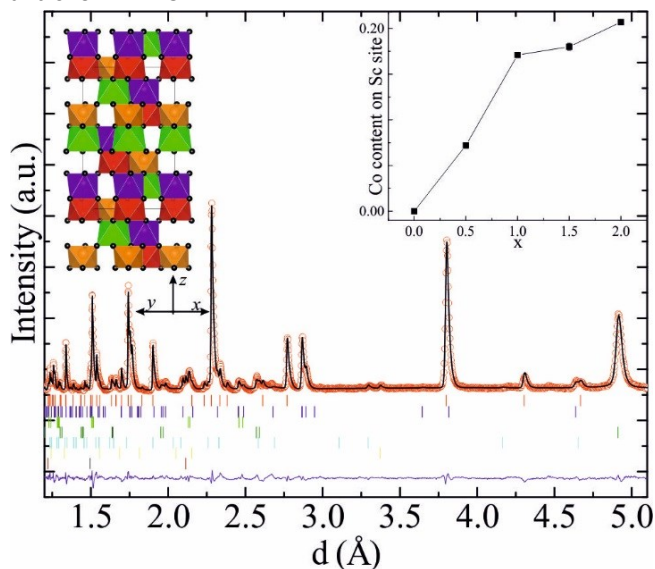
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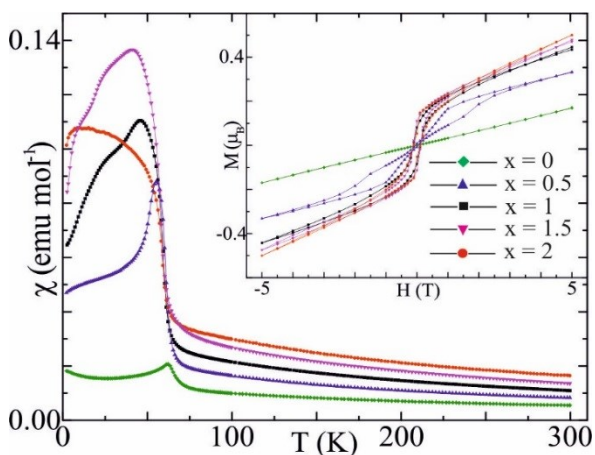
† Electronic Supplementary Information (ESI) available: Supporting experimental details, figures and tables. See DOI: 10.1039/x0xx00000x

previous study,<sup>13</sup> 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.



**Fig. 1.** Rietveld fit to the 100 K NPD data of  $\text{Co}_2\text{ScSbO}_6$ . Additional Bragg marks identify secondary  $\text{Sc}_{5.5}\text{Sb}_{1.5}\text{O}_{12}$  (9.4%),  $\text{CoO}$  (7.8%),  $\text{CoSb}_2\text{O}_6$  (3%) and the magnetic reflections of  $\text{CoO}$ . The insets show the structural model (Co1, Co2, Sc and Sb depicted in green, red, blue and orange respectively) and the evolution of the proportion of Co at the Sc site with  $x$ .

ZFC magnetic susceptibility measurements and magnetization-field loops at 2 K are shown in Fig. 2.  $\text{Co}_2\text{ScSbO}_6$  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  $\text{Co}^{2+}$ . Similar values  $\approx 5.20 \mu_B$  have been reported for other  $\text{Co}^{2+}$  oxides with a strong  $^4T_{1g}$  excited state orbital contribution to the moment.<sup>18-19</sup>



**Fig. 2.** ZFC magnetic susceptibility data of  $\text{Ni}_{2-x}\text{Co}_x\text{ScSbO}_6$  under a magnetic field of 1 T. Field dependence of the magnetization at 2 K shown in the inset.

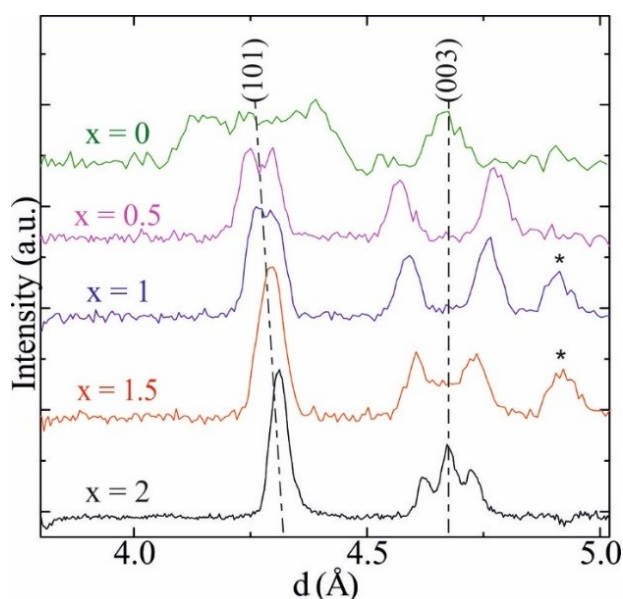
The other  $\text{Ni}_{2-x}\text{Co}_x\text{ScSbO}_6$  compositions also have magnetic transitions near 60 K. Curie-Weiss fitting results, summarized in Table 1, show that all of the effective magnetic moments are close to calculated values for the corresponding proportions of spin only  $\text{Ni}^{2+}$  ( $\mu_{\text{eff}} = 2.83 \mu_B$ ) and  $\text{Co}^{2+}$  ( $\mu_{\text{eff}} = 5.20 \mu_B$  is assumed).  $M$ - $H$  loops show a change in the bulk magnetic properties as Co is introduced.  $x = 0$   $\text{Ni}_2\text{ScSbO}_6$  is antiferromagnetic with linear  $M$ - $H$  but  $x = 1$  and 1.5 samples have a similar ferrimagnetic behaviour to  $\text{Co}_2\text{ScSbO}_6$ , 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  $\text{Ni}_{2-x}\text{Co}_x\text{ScSbO}_6$  materials;  $T_C$ , Weiss constant ( $\theta$ ), effective moments ( $\mu_{\text{eff}}$ ), critical field ( $H_c$ ) and spontaneous magnetization at 2 K ( $M_s$ ) determined from magnetic measurements (top); ordered moment ( $\mu$ ), refined propagation vector component ( $k_i = k_y$  for  $x = 0$ ,  $k_i = k_z$  for  $x \neq 0$ ),  $1/3n$  periodicity for integer  $n$ , and % of the  $[00k_z]$  magnetic phase coexisting with  $[000]$  for  $x = 1.5$  and 2 (bottom).

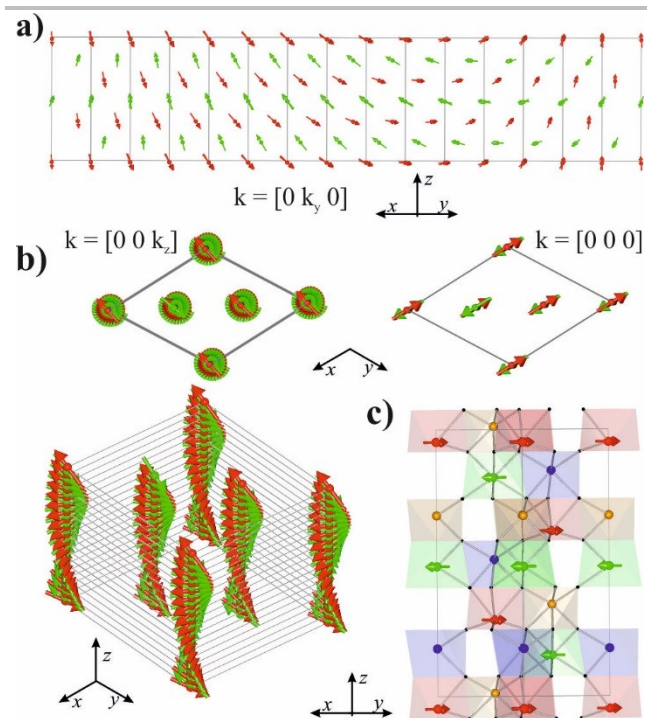
$x$	0	0.5	1	1.5	2
$T_C$ (K)	65	61	59	58	59
$\theta$ (K)	-144	-104	-105	-106	-142
$\mu_{\text{eff}}$ ( $\mu_B$ )	4.41	5.18	5.97	6.66	7.61
$\mu_{\text{th}}$ ( $\mu_B$ )	4.00	5.05	5.92	6.68	7.35
$H_c$ (T)	-	1.5	0.7	-	-
$M_s$ ( $\mu_B$ )	-	0.15	0.2	0.22	0.14
$\mu$ ( $\mu_B$ )	1.72(3)	2.18(2)	2.40(1)	2.63(3)	2.94(1)
$\mu_{\text{th}}$ ( $\mu_B$ )	2.00	2.25	2.50	2.75	3.00
$k_i$	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
% $[00k_z]$	-	100	100	84.8(1)	63.4(1)

Figure 3 shows the evolution of the principal magnetic diffraction contributions in the  $\text{Ni}_{2-x}\text{Co}_x\text{ScSbO}_6$  series, obtained by subtracting the 100 K from the 4K NPD profiles (collected from WISH@ISIS for  $x = 2$ ; SPODI@FRMII for  $x \neq 2$ ).  $x = 0$   $\text{Ni}_2\text{ScSbO}_6$  has prominent magnetic satellite reflections around the (101) peak and a magnetic (003) peak, which arise from an incommensurate  $[0 k_y 0]$  magnetic propagation vector. As noted previously,<sup>13</sup> 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  $\text{Co}^{2+}$  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  $n = 10$   $\text{Co}_2\text{ScSbO}_6$ ), as discussed later.



**Fig. 3.** Difference (4 K – 100 K) NPD patterns of  $\text{Ni}_{2-x}\text{Co}_x\text{ScSbO}_6$  showing magnetic peaks. (003) and (101) peak positions are marked with dashed lines. Magnetic peaks from impurity  $\text{Co}_{2.33}\text{Sb}_{0.64}\text{O}_4$  are identified with an asterisk.



**Fig. 4.** Magnetic structures of  $\text{Ni}_{2-x}\text{Co}_x\text{ScSbO}_6$  for a)  $x = 0$  with propagation vector  $k = [0 k_y, 0]$ , b)  $x = 0.5$  to 2 with  $k = [0 0 k_z]$  and c) the competing commensurate  $k = [0 0 0]$  phase for  $x = 1.5$  and 2. Green and red arrows represent the  $\text{Ni}^{2+}/\text{Co}^{2+}$  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  $[0 0 k_z]$  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  $[0 0 k_z]$  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  $[0 0 k_z]$  and  $[0 0 0]$  phases gives a saturation value of  $2.94(1) \mu_B$  for  $\text{Co}_2\text{ScSbO}_6$  at 1.7 K, close to the ideal spin-only value of  $3.00 \mu_B$ , and  $[0 0 k_z]:[0 0 0]$  phase proportions of 63 : 37. No changes to the magnetic order are found up to  $T_C$  for any of the  $\text{Ni}_{2-x}\text{Co}_x\text{ScSbO}_6$  materials. Furthermore, proportions of coexisting  $[0 0 k_z]$  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  $\text{Co}_2\text{ScSbO}_6$  in Fig. 5a, with further refinement results in ESI.

These results demonstrate a very rich magnetic behaviour in the  $\text{Ni}_{2-x}\text{Co}_x\text{ScSbO}_6$  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  $\text{Co}^{2+}$  confines spins to the  $xy$  plane for all Co-containing materials. This switches magnetic order from the incommensurate  $[0 k_y 0]$  type previously reported for  $\text{Ni}_2\text{ScSbO}_6$  to a new  $[0 0 k_z]$  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  $k_z$ .

Although the balance of NN and NNN couplings may favour incommensurate periodicities, the strong anisotropy of  $\text{Co}^{2+}$  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  $\text{Ni}_{2-x}\text{Co}_x\text{ScSbO}_6$  compositions will be needed to explore the full variety of spin structures. Lock-in orders are reported in other  $\text{Co}^{2+}$  oxides such as  $\text{CoCr}_2\text{O}_4$ <sup>20</sup> and  $\text{Co}_3\text{V}_2\text{O}_8$ <sup>21</sup>, but the  $\text{Ni}_{2-x}\text{Co}_x\text{ScSbO}_6$  series represents an unusually rich series of lock-in phases accessible through chemical tuning at zero field strength.

The R3 lattice symmetry of the  $\text{Ni}_{2-x}\text{Co}_x\text{ScSbO}_6$  materials allows linear or bilinear magnetoelectric effects, making these materials potential multiferroics. The electric polarisation, calculated to be in the range  $E_0 = 13\text{--}20 \mu\text{C cm}^{-2}$ , 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  $[0\ 0\ k_z]$  helical phases. The  $[0\ 0\ 0]$  phase has net magnetisation in the  $xy$  plane and so a perpendicular coupling mechanism between  $M_0$  and  $E_0$  may operate, as discussed for polar  $\text{MnTiO}_3$ <sup>22</sup>. Canting of the spins in the  $[0\ 0\ 0]$  or  $[0\ 0\ k_z]$  phases to give a small magnetization parallel to  $E_0$  may also result from antisymmetric Dzyaloshinskii-Moriya coupling.

incommensurate  $[0\ k_y\ 0]$  phase for pure  $\text{Ni}_2\text{ScSbO}_6$  to a series of long-period lock-in  $[0\ 0\ k_z]$  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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Data for this study have been deposited at <https://datashare.is.ed.ac.uk/handle/10283/838>.

### Conflicts of interest

There are no conflicts of interest to declare.

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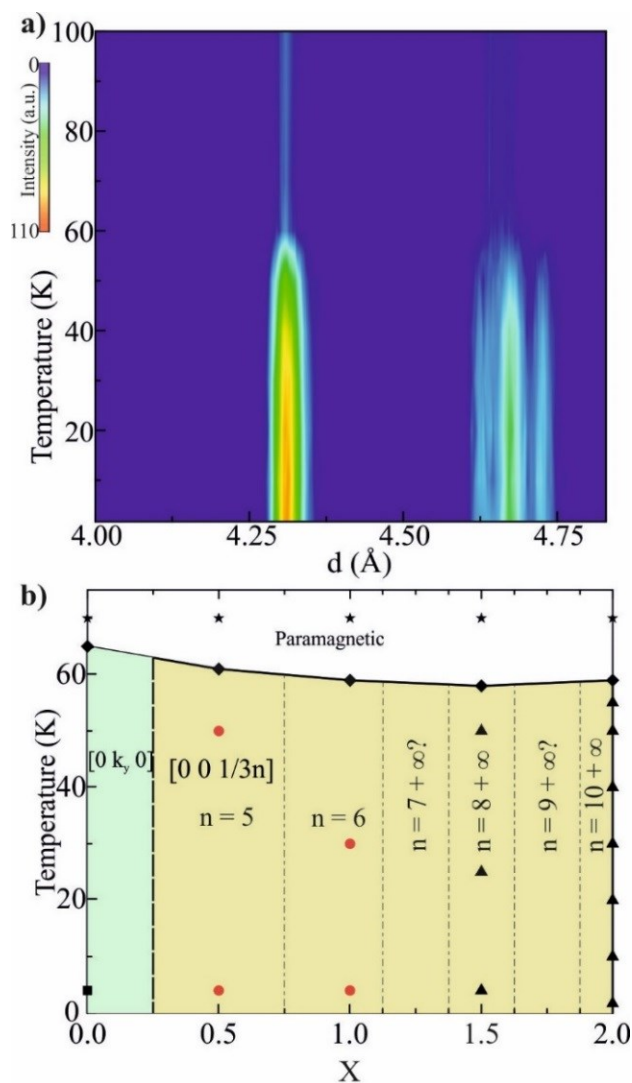


Fig. 5. a) Thermodiffraction neutron data for  $\text{Co}_2\text{ScSbO}_6$  showing that  $[0\ 0\ 0]$  and  $[0\ 0\ k_z]$  magnetic phases (evidenced by peaks at 4.7 and 4.3 Å respectively) coexist at all temperatures below  $T_C = 60$  K. b) Magnetic phase diagram of  $\text{Ni}_{2-x}\text{Co}_x\text{ScSbO}_6$  system.  $n$  values show the observed and postulated (marked '?')  $[0\ 0\ 1/3n]$  lock-in phases. Star/rhombus/square/circle/triangle symbols refer to paramagnetic phase/ $T_C$ / $[0\ k_y\ 0]$ / $[0\ 0\ k_z]$ / $[0\ 0\ k_z]$ + $[0\ 0\ 0]$  observations.

In conclusion, a new oxide  $\text{Co}_2\text{ScSbO}_6$  has been synthesised at 6 GPa, and solid solutions  $\text{Ni}_{2-x}\text{Co}_x\text{ScSbO}_6$  ( $x = 0 - 1.5$ ) were prepared at ambient pressure. All compositions adopt the  $\text{Ni}_3\text{TeO}_6$ -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