Electronic Supplementary Information for the paper

Orbitally induced hierarchy of exchange interactions in zigzag antiferromagnetic state of honeycomb silver delafossite $Ag_3Co_2SbO_6$

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Contents

Table S1. Known $Ag_3M_2RO_6$ and Ag_3MRXO_6 delafossite-related mixed oxides

Only Ag_2SnO_3 [42, 43] has been prepared by direct synthesis and characterized by single-crystal diffraction. All other compounds have been prepared by ion exchange from the sodium or lithium counterparts; they exhibit very similar powder diffraction patterns typical of the rhombohedral $AgFeO_2$ type; almost all show one or two weak and diffuse superstructure reflection; however, interpretations of these patterns are different.

Composition	Comments
$Ag_3(AgSn_2)O_6$ [42, 43]	The basic structure is double-layered $P6_322$ honeycomb type, but there is an incommensurate modulation with a = 29.22 Å.
$Ag_3LiTi_2O_6$ [44]	Powder pattern indexed as a trigonal superstructure. No structure refinement.
$Ag_3M_2SbO_6$ (M = Ni, Zn) [31]	No superlattice reflections found. The structures were refined within disordered $Ag(M_{2/3}Sb_{1/3})O_2$ $R\bar{3}m$ model, although the authors assumed high degree of local order.
$Ag_3LiM_2O_6$ (M = Ti, Sn) [45]	No indexing; disordered $Ag(Li_{1/3}M_{2/3})O_2$ formulas were used although one or two superlattice reflections were visible.
$Ag_3Co_2SbO_6$ [46]	The superstructure was refined within the trigonal $P3_112$ model. However, accuracy was low, and monoclinic symmetry could not be excluded as discussed in the present paper.
$Ag_3LiRu_2O_6$ [47]	Paradoxically, superstructure was refined omitting the unique superstructure reflection; monoclinic C2/m model was used although no splitting of reflections from the rhombohedral subcell was detected. It was assumed that each layer was ordered but their stacking was disordered.
$Ag_3LiRu_2O_6$ [48]	No superlattice reflections found. The structure was refined within disordered $Ag(Li_{1/3}Ru_{2/3})O_2$ $R\bar{3}m$ model. Lattice parameters differ significantly (by 2.0-2.4%) from the subcell parameters in the preceding work [42].
$Ag_3LiM_2O_6$ (M = Rh, Ir) [49]	Superlattice reflections were found in both X-ray and electron diffraction. Each layer is assumed to be fully ordered. However, the structures were refined within disordered $Ag(Li_{1/3}M_{2/3})O_2$ $R\bar{3}m$ model.
$Ag_3Ni_2BiO_6$ [50]	Indexed as a trigonal superstructure ($P3_112$). No structure refinement.
$Ag_3NaFeSbO_6$ [51]	Indexed as a trigonal superstructure ($P3_112$). Structural model was depicted but not refined.
$Ag_3LiMTeO_6$ (M = Co, Ni, Zn) [52], $Ag_3LiMnSbO_6$ [53]	Superlattice reflections are visible but not discussed. No indexing, no lattice parameters.
$Ag_3LiMSbO_6$ (M = Al, Cr, Fe, Ga) [53]	Indexed as a trigonal superstructure ($P3_112$). No structure refinement.

Table S2. Experimental and refinement details for $Ag_3M_2SbO_6$ (M = Co, Zn)

Formula	$Ag_3Co_2SbO_6$	$Ag_3Zn_2SbO_6$
Formula weight	659.2	672.1
Crystal system	monoclinic	monoclinic
Space group	C2/m	C2/m
Z	2	2
a, Å	5.3770(13)	5.3829(2)
b, Å	9.3118(22)	9.3102(3)
c, Å	6.4810(14)	6.5046(2)
β, °	106.512(7)	106.306(4)
V, Å^3	311.12(2)	312.87(2)
Sample preparation	Amorphous admixture (beryllium carbonate or coffee) to reduce texture	
Diffractometer	Rigaku D/max-RC	ARL X'tra
Diffraction geometry	Bragg-Brentano	
Wavelength selection	Secondary-beam monochromator	Solid-state Si(Li) detector
Wavelength (CuKα), Å	1.5406, 1.5444	
U, kV	55	40
I, mA	180	40
Receiving slit, mm	0.3	0.4
Angular range, °	10–100	12–101.4
Step size, °	0.02	0.02
Count time, s	3	2.4
Number of data points	4500	4470
Number of hkl	179	179
Number of variables	55	57
R_{wp}	0.0769	0.0605
R_{exp}	0.0276	0.0423
R_F^2	0.0198	0.0228
χ^2	7.830	2.067

Table S3. Atomic coordinates, site occupancies and thermal displacement parameters for $Ag_3M_2SbO_6$ (M = Co, Zn)

	$Ag_3Co_2SbO_6$					$Ag_3Zn_2SbO_6$				
Atom	x	y	z	sof	Uiso	x	y	z	sof	Uiso
Sb1	0	0	0	0.458(23)	0.016(4)	0	0	0	0.358(7)	0.0203(9)
M1	0	0	0	0.542(23)	0.016(4)	0	0	0	0.642(7)	0.0203(9)
M2	0	0.6661(10)	0	0.729(11)	0.022(4)	0	0.6688(4)	0	0.679(3)	0.0251(5)
Sb2	0	0.6661(10)	0	0.271(11)	0.022(4)	0	0.6688(4)	0	0.321(3)	0.0251(5)
Ag1	0	1/2	1/2	0.962(12)	0.016(3)	0	1/2	1/2	0.977(3)	0.0131(5)
Ag2	1/2	0.3426(6)	1/2	0.927(7)	0.006(3)	1/2	0.3413(3)	1/2	0.9423(16)	0.0183(3)
O1	0.618(5)	0.364(2)	0.827(4)	1	0.01	0.598(3)	0.3695(6)	0.8258(10)	1	0.01
O2	0.833(7)	1/2	0.173(8)	1	0.01	0.846(3)	1/2	0.1736(18)	1	0.01

Comments. The authors assume that the reported M/Sb mixing is fictitious due to multiple stacking faults whereas each individual layer is essentially ordered with site 1 occupied by Sb only and site 2, by M^{2+} only. Displacement parameters for O1 and O2 were fixed to prevent instability and negative values during the structure refinement process.

Table S4. Important interatomic distances (Å) and bond angles (°) in $Ag_3M_2SbO_6$ (M = Co, Zn)

	$Ag_3Co_2SbO_6$	$Ag_3Zn_2SbO_6$
M1-O2	1.82(3)×2	1.888(13)×2
-O1	1.92(3)×4	1.837(9)×4
average	1.88	1.85
M2-O1	2.06(2)×2	2.171(12)×2
-O2	2.24(4)×2	2.227(11)×2
-O1	2.34(2)×2	2.322(8)×2
Average	2.21	2.24
Ag1-O2	2.05(5)×2	2.051(11)×2
Ag2-O1	2.04(2)×2	2.052(6)×2
O2-Ag1-O2	180.0	180.0
O1-Ag2-O1	168.8(10)	165.3(2)
M1-O1-M2	102.5 (11)	101.7(4)
M1-O1-M2	93.5(7)	95.0(2)
M2-O1-M2	89.8(9)	86.7(3)
M1-O2-M2	98.94(2)×2	98.159(2)×2
M2-O2-M2	87.22(1)	89.791(1)

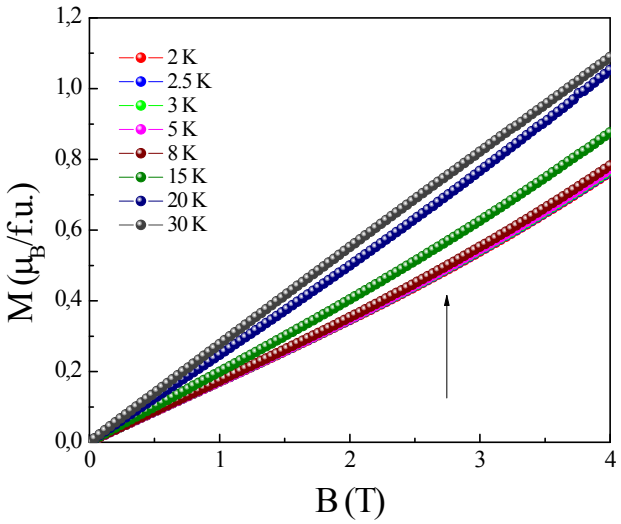

Fig. S1. The magnetization curves for $Ag_3Co_2SbO_6$ at various temperatures.

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