# Rare-earth chalcogenides: A large family of triangular lattice spin liquid candidates

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#### **Abstract**

Quantum spin-frustrated materials are expected to host many exotic quantum spin states like quantum spin liquid (QSL), and have attracted numerous interest in condensed matter physics. The discovery of YbMgGaO4 invokes increasing attention on rare-earthbased spin frustrated materials with strong spin-orbit coupling. Here we report the discovery of a large family of quantum spin liquid candidates. We have systematically synthesized rare-earth chalcogenides AReCh2 (A=alkali or monovalent ions, Re=rare earth, Ch=O, S, Se), and made structural and thermodynamics characterizations. The family compounds possess the structure of delafossite with a high symmetry of R-3m, and antiferromagnetically coupled magnetic ions form perfect triangular layers which are well separated along c-axis. The Curie-Weiss temperatures range from several to more than 100 kelvins. Specific heat and magnetic susceptibility down to 50 mK on NaYbO<sub>2</sub>, NaYbS2 and NaYbSe2 single crystals and polycrystals, reveal no structural or magnetic transition even at the lowest measurement temperature. The family, having the simplest structure and chemical formula among the known QSL candidates, removes the issue on disorder raised in YbMgGaO4. And most excitingly, the rich diversity of the family members allows tunable charge gaps, selectable exchange coupling, and many other advantages. This makes the family an ideal platform for fundamental research of QSL and its promising applications.

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#### Introduction

The concept of quantum spin liquid was proposed by P. W. Anderson over 40 years ago<sup>[1]</sup>. It describes a novel highly entangled spin state and was initially constructed with a superposition of spin singlets on the triangular antiferromagnet, so-called resonating-valence-bond model<sup>[1]</sup>. Later on, the ultimate connection between QSL and high-temperature superconductivity was theoretically established through doping a QSL<sup>[2]</sup>. The underlying topological properties in QSL were carefully studied and classified by X. G. Wen et al<sup>[3-4]</sup>. Kitaev further demonstrated that such topological phases can be employed for the high-fidelity quantum computation<sup>[5]</sup>. This has stimulated intensive interest in searching for QSL materials.

Quantum spin frustrated materials, particularly the spin-triangle-based antiferromagnets with strong geometrical frustration<sup>[6]</sup>, were considered to be the most likely systems realizing QSL. So far, a number of compounds have been reported to host QSL. Among them, the well-known examples include herbersmithite and its derived compounds<sup>[7-11]</sup>, and triangular organics<sup>[12]</sup>. The magnetic ions in most of the compounds are 3d transition metal ions Cu<sup>2+</sup> with S=1/2, which is crucial to strengthen quantum fluctuations.

On the other hand, the spin frustrated materials containing magnetic rare-earth ions are also considered to be possible QSL candidates<sup>[13]</sup>. The spin ground state for the rare-earth ions with an odd number of f electrons (not including Gd<sup>3+</sup>), is a Kramers doublet which can be mapped to a well-defined effective S=1/2 spin and is protected by time reversal symmetry and crystal fields<sup>[14]</sup>. In many cases the non-Kramers rare-earth ions can also be taken as effective S=1/2 systems at low temperatures, though lacking the protection by time reversal symmetry<sup>[15-16]</sup>. Therefore, rare-earth based spin-frustrated materials plays a crucial role in the exploration of QSL candidates<sup>[13]</sup>. In fact, some QSL behaviors have been reported in several pyrochlore and spinel compounds<sup>[17-21]</sup>.

The discovery of YbMgGaO<sub>4</sub> has invoked increasing interest in searching for rare-earth based spin-frustrated materials<sup>[22]</sup>. The compound has a high symmetry of R-3m and Yb<sup>3+</sup> ions form a flat and perfect triangular lattice<sup>[22-23]</sup>. The availability of high-quality single crystals allows extensive and deep studies of magnetic properties using neutron scattering<sup>[24-27]</sup>, muon spin relaxation (muSR)<sup>[28]</sup>, nuclear spin resonance (NMR), electron spin resonance (ESR)<sup>[34]</sup> etc. The studies point to the possibility of gapless QSL ground state<sup>[23-24][28-29]</sup>. On the other hand, some experiments and theoretical arguments raised the

issue on Ga/Mg disorder, which was proposed to be responsible for the spin ground state and/or QSL stability [22],[30-32]. The small exchange coupling (J  $\sim$  1 K) allows to easily tune the spin state with a laboratory magnetic field [22-23,29]. Meanwhile, it also requires that most experiments must be carried out at ultralow temperatures [29,33]. In some cases this could be an obstacle for in-depth studies and possible applications.

As mentioned above, there is a long list of numerous rare-earth spin-frustrated materials<sup>[2,13]</sup>. Then the question is if one can find out some compounds or systems with larger exchange couplings and without disorder<sup>[6]</sup>. That is what we have done in this work. We systematically synthesized rare-earth based delafossite AReCh<sub>2</sub> (A=alkali or monovalent ions, Re=rare earth, Ch=O, S, Se) and made structural and thermodynamic characterizations. The compounds have a high symmetry of R-3m and perfect spin triangular layers<sup>[35-36]</sup>. The magnetic measurements indicate that spins are antiferromagnetically coupled in all the compounds and the Weiss temperatures vary from several to over 100 K. For the representative NaYbCh<sub>2</sub> (Ch=O, S, Se) samples, no magnetic ordering or transition is observed in the specific heat and susceptibility measurements down to 50 mK. Thus, this is a large family of QSL candidates with the simplest structure and chemical formula so far. Its crystal structure naturally removes the issue on Ga/Mg disorder proposed in YbMgGaO<sub>4</sub>. The diversity of the large family makes it an ideal playground for studying QSL and exploring its promising applications.

### Sample preparation and experimental methods

The polycrystals of  $NaLnO_2(Ln = Yb, Lu)$  were synthesized by the method of solid-state reaction under high temperatures:

$$Na_2CO_3 + Ln_2O_3 \rightarrow 2NaLnO_2 + O_2$$
 (Ln=Yb, Lu).

Na<sub>2</sub>CO<sub>3</sub> and Ln<sub>2</sub>O<sub>3</sub> powders were mixed in a dry process (mixing molar ratio: Na<sub>2</sub>O: Yb<sub>2</sub>O<sub>3</sub> = 2.5:1) and shaped into a pellet by isostatic pressing (50 MPa, 2 min). Shaped samples were heated at 900°C for 9 hours. After the heating, the samples were grinded and washed with distilled water and ethanol, at last dried in air at room temperature for 48 hours.

The polycrystals of NaLnS<sub>2</sub> (Ln=La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) were synthesized by the method of solid-state reaction under high temperature: Na<sub>2</sub>S + 2Ln + 3S  $\rightarrow$  2NaLnS<sub>2</sub> (Ln = Lu, Se, Tm, Er, Ho, Dy, Tb, Gd, Eu, Sm, Nd, Pr, Ce, La) Na<sub>2</sub>S, Yb and S powder was mixed in Ar environment glove box. The mixed powders were

placed in a graphite crucible and vacuum packaged with quartz tube. Packaged samples were heated at 850°C for 48 hours. After the heating, the sample were powder and washed with distilled water and then dried in air at 50 °C for 6 hours. The synthesis of polycrystals of NaLnSe<sub>2</sub> (Ln =Er, Yb, Lu) were similar with the synthesis of powders of NaLnS<sub>2</sub>. The temperature was adjusted to 900°C.

We have also successfully grown high quality NaYbSe<sub>2</sub> single crystals. The growth conditions of single crystals are more rigorous than NaYbSe<sub>2</sub> polycrystals. Na<sub>2</sub>Se, Yb and Se powder were mixed in Ar environment glove box (mixing molar ratio: Na<sub>2</sub>Se: Yb : Se = 1 :2 :12). The mixed powder was placed in special quartz tube that can withstand higher pressure. Packaged samples were headed at 1000°C for 48 hours. After the heating, we can observe 2-3 mm size single crystals.

Powder XRD profiles were measured with Bruker-D8 by step scanning. The TOPAS program was used for Rietveld crystal structure refinements. The temperature dependence of magnetic susceptibility from 1.8K to 300K was measured with a SQUID magnetometer (Quantum Design Magnetic Property Measurement System, MPMS) under both ZFC and FC for all the samples with the brass sample holder. The AC susceptibility measurements from 50mK to 4K were performed using a dilution refrigeration system (DR). The polycrystalline sample was pressed into a thin plate and fixed on a sample holder with GE vanish. The heat capacity measurements from 2K to 30K were performed using PPMS (Quantum Design Physical Property Measurement System) and DR was employed for the measurements from 50mK to 4K. The plate sample was mounted on a sample holder with N grease for better thermal contact.

#### **Results and discussions**

Fig. 1 shows the crystal structure of rare-earth delafossite and the Rietveld refinements for three representative samples NaYbO<sub>2</sub>, NaYbS<sub>2</sub> and NaYbSe<sub>2</sub> (Detailed structural information extracted from the refinements can be found in Supplementary Materials). Under the high symmetry of R-3m, magnetic ions form flat triangular layers which are well separated. ReCh<sub>6</sub> octahedra are connected by edge-sharing. The local crystal-field environment around magnetic ions is exactly analogous to the case of YbMgGaO<sub>4</sub>. Therefore, one may expect a crystal-field splitting of Yb<sup>3+</sup> ions similar to that in YbMgGaO<sub>4</sub>. That means an effective S=1/2 spin is strictly held in this case. And similar to YbMgGaO<sub>4</sub>, Dzyaloshinskii-Moriya (DM) interaction is also cancelled in this case.

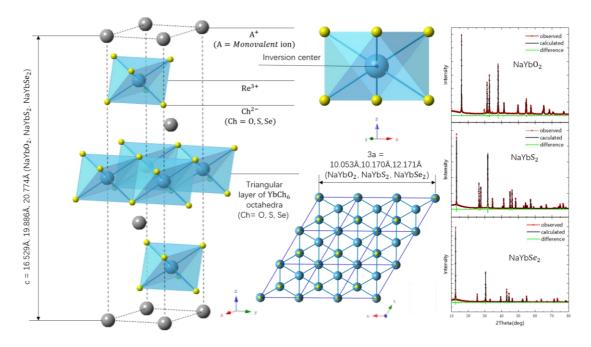


Fig. 1 General crystal structure of rare-earth chalcogenides and the powder diffraction patterns and Rietveld refinements for NaYbCh<sub>2</sub> (Ch=O, S, Se)

The Mg/Ga disorder in YbMgGaO<sub>4</sub> has been extensively discussed and is still under debate. In some experiments and theoretical calculations, the disorder was considered to play a dominant role in stabilizing QSL state and contributing to low-energy excitations. For comparison, there is no longer such a disorder in the family of rare-earth chalcogenides, due to the structural simplicity and high symmetry. The issue on disorder is completely removed in the family. We further made the analysis of element ratio (See Supplementary Materials), which is close to the nominal ratio. This rules out the possibility of the disorder caused by element deficiency. If one concerns about the active monovalent ions like Na<sup>+</sup> and K<sup>+</sup>, he still has plenty of choices of the heavy monovalent ones like Rb<sup>+</sup>, Cs<sup>+</sup>, Cu<sup>+</sup> and Ag<sup>+</sup>, etc.

For the selected sub-family NaYbCh<sub>2</sub> (Ch=O, S, Se), we measured DC magnetic susceptibility in the range of 2-300 K and AC susceptibility from 50mK to 4 K, which are presented in Fig. 2. The Curie-Weiss (CW) fitting was made from 150 to 300K according to the crystal-field splitting in YbMgGaO<sub>4</sub> and the fitting results are summarized in Table I. The negative CW temperatures suggest an antiferromagnetic coupling in all the samples. Excitingly, the CW temperatures are much larger than that of YbMgGaO<sub>4</sub> because of the smaller distances between nearest-neighbor Yb<sup>3+</sup> in rare-earth chalcogenides. AC susceptibility for the three samples shows no sign of long-range

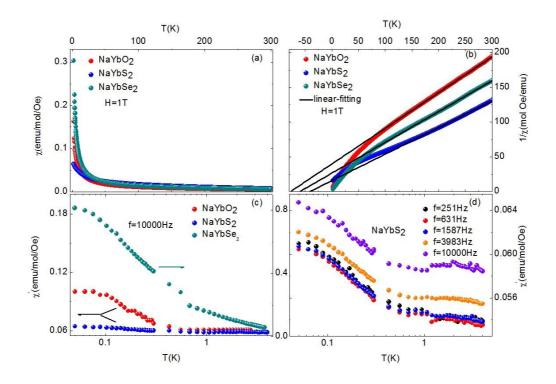


Fig. 2 DC (a & b) and AC (c & d) magnetic susceptibility of polycrystalline NaYbCh<sub>2</sub> (Ch=O, S, Se).

magnetic ordering. The measurements under various frequencies further confirms that there is no spin freezing either. Interestingly, the susceptibility saturation with down to zero temperature is clearly seen for all the three samples. This should be one of the consequences caused by strong spin-orbit coupling rather than a sign of finite spin excitations. The susceptibility of NaYbSe<sub>2</sub> at low temperatures is obviously larger than that of the other two compounds. In fact, the distance between nearest neighboring Yb<sup>3+</sup> ions in NaYbSe<sub>2</sub> is also larger, while its CW temperatures and moment obtained from the CW fitting look comparable to the other two. The reason for this is unclear at the moment.

Table I Parameters extracted from Curie-Weiss fitting for NaYbCh<sub>2</sub> (Ch=O, S, Se)

Ch	Space group	С	$ heta_{\scriptscriptstyle CW}$ / $K$	$\mu_{\it eff}$
0	R-3m	1.9448	-77.35	3.94
S	R-3m	2.6166	-40.98	4.57
Se	R-3m	2.2550	-59.84	4.24

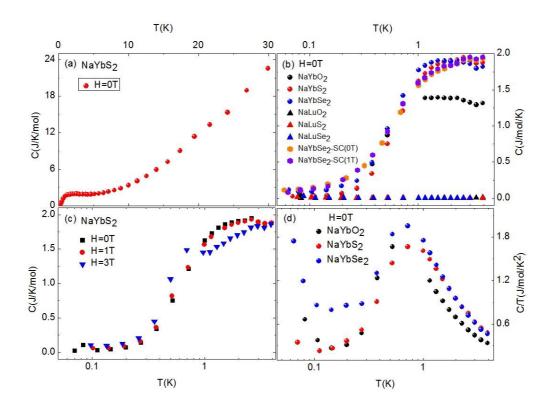


Fig. 3 Specific heat measurements on NaYbCh<sub>2</sub> (Ch=O, S, Se). Single crystal NaYbSe<sub>2</sub> and polycrystalline NaYbO<sub>2</sub> and NaYbS<sub>2</sub> were used in the measurements.

Specific heat results are shown in Fig. 3. There is no obvious transition down to 50 mK in the compounds, and it is consistent with the conclusion from the susceptibility experiments. We observed no apparent change or shift with applying a magnetic field up to 3 T (Fig. 3c). On the other hand, an upturn is seen below 100 mK in the C/T~T plot (Fig. 3d). This may be contributed by nuclear spins. The upturn actually makes it hard to see the intrinsic trend of specific heat below 100 mK and to conclude that the spin ground state is gapless or gapped QSL. More magnetic and thermodynamics experiments are required in the future.

Here it should be pointed out that there is no obvious disorder in the present case and we still observed no long-range magnetic ordering or freezing which points to a possible QSL ground state. This means that the rare-earth triangular system, including rare-earth chalcogenides reported here and YbMgGaO<sub>4</sub>, intrinsically hosts QSL state which is not stabilized by or even originated from the Ga/Mg charge disorder.

The measurements discussed above are based on the sub-family NaYbCh<sub>2</sub>(Ch=O, S, Se). Towards a comprehensive view of the large family, we fixed Na and S, and

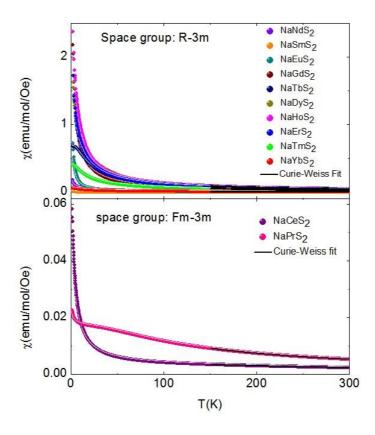


Fig. 4 Magnetic susceptibility of NaReS<sub>2</sub> (Re=Ce-Yb) in the range of 2 to 300 K.

systematically synthesized the other sub-family NaReS<sub>2</sub> (Re=La - Lu). The Rietveld refinements for all the fourteen compounds have been made and the detailed structural parameters can be found in the Supplementary Materials. The family members from Nd to Lu, keep the high-symmetry of R-3m. But the three end-members, NaLaS<sub>2</sub>, NaCeS<sub>2</sub> and NaPrS<sub>2</sub> show a cubic structure with the symmetry of Fm-3m. Obviously this is caused by the larger ionic radii of La, Ce and Pr. The magnetic susceptibility measurements from 2 to 300 K have been carried out on the sub-family and the results are shown in Fig. 4. No obvious magnetic transition can be seen in all the compounds with R-3m symmetry. Similar to the R-3m brothers, the cubic NaCeS<sub>2</sub> also shows no sign of magnetic transition from 2 to 300 K, as the perfect triangular lattice formed by magnetic ions remains undistorted and the strong geometrical frustration is always there. However, an anomaly appears around 10 K in the susceptibility of NaPrS<sub>2</sub> (Fm-3m).

Table II Parameters extracted from the Curie-Weiss fitting for NaReS<sub>2</sub> (Re=Ce-Yb)

Re	Space group	С	$\theta_{\scriptscriptstyle CW}$ / $K$	$\mu_{\it eff}$	
				$Obs.(\mu_B)$	$Cal.(\mu_{\scriptscriptstyle B})$
Се	Fm-3m	1.1145	-164.42	2.99	2.54
Pr	Fm-3m	1.91757	-57.48	3.92	3.58
Nd	R-3m	1.78198	-25.35	3.77	3.62
Sm	R-3m	0.71761	-343.05	2.40	0.84
Eu	R-3m	3.19082	-106.13	5.05	3.6
Gd	R-3m	8.5521	-1.98	8.27	7.94
Tb	R-3m	12.87953	-9.49	10.15	9.72
Dy	R-3m	14.55906	-9.39	10.79	10.63
Но	R-3m	13.8468	-5.90	10.52	10.60
Er	R-3m	12.13713	-4.62	9.85	9.59
Tm	R-3m	7.40589	-3.83	7.69	7.57
Yb	R-3m	2.90963	-63.74	4.82	4.54

The CW fitting was made from 150 to 300 K, assuming a reasonably high crystal-field splitting. The fitting results can be found in Table II. We can see that the exchange coupling changes from sample to sample. In other words, we have the opportunity to select the compounds with various exchange coupling. Beyond this, one can further tune the charge gaps of the family members by element substitution. The absorption spectra (see Supplementary Materials) indicate that the charge gaps are roughly 4.5 eV, 2.7 eV and 1.9 eV for NaYbO<sub>2</sub>, NaYbS<sub>2</sub>, and NaYbSe<sub>2</sub>, respectively. These exciting advantages stem from the rich diversity of the family. In fact, we have made a careful literature research and found that most of the family members have the high-symmetry of R-3m and hence are potential QSL materials (see Supplementary Materials). This suggests that the family is an ideal playground, on which we can tune the basic material parameters or exchange coupling to explore QSL and develop its possible applications.

#### **Summary**

In this work, we synthesized rare-earth chalcogenides AReCh<sub>2</sub> which has a delafossite structure, and made structural and thermodynamics characterizations. The family has a high symmetry of R-3m, and magnetic ions are antiferromagnetically coupled and form

perfect triangular layers. The Curie-Weiss temperatures vary in the range of 4 K to over 100 K. Magnetic susceptibility and specific heat measurements down to 50 mK indicate no sign of long-range magnetic ordering or transition. The family removes the disorder issue raised in YbMgGaO<sub>4</sub>. The unique advantages, such as various charge gaps and exchange coupling, suggest that the family may be an ideal platform for the study of QSL.

## Acknowledgements

We are grateful to Gang Chen for inspiring discussions. We thank Zicheng Wen for assisting absorption measurements. This work was supported by the Ministry of Science and Technology of China (2016YFA0300504 & 2017YFA0302904) and the NSF of China (11774419 & 11474357).

#### **Author contributions**

Q.M.Z proposed the original ideas and directed the whole study. W.W.L made NaLnS<sub>2</sub> polycrystals and grew NaYbS<sub>2</sub> single crystals, made structural refinement, and made specific heat and magnetic measurements and analysis. Z. Z synthesized NaYbSe<sub>2</sub> and NaLuSe<sub>2</sub> polycrystals and made refinement, and grew NaYbSe<sub>2</sub> single crystals. J.T.J synthesized NaYbO<sub>2</sub> and NaLuO<sub>2</sub> polycrystals and made structural characterizations. Y.X.L and H.C.L grew NaYbSe<sub>2</sub> single crystals. H.C.L assisted crystal growth.

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# **Supplementary Materials**

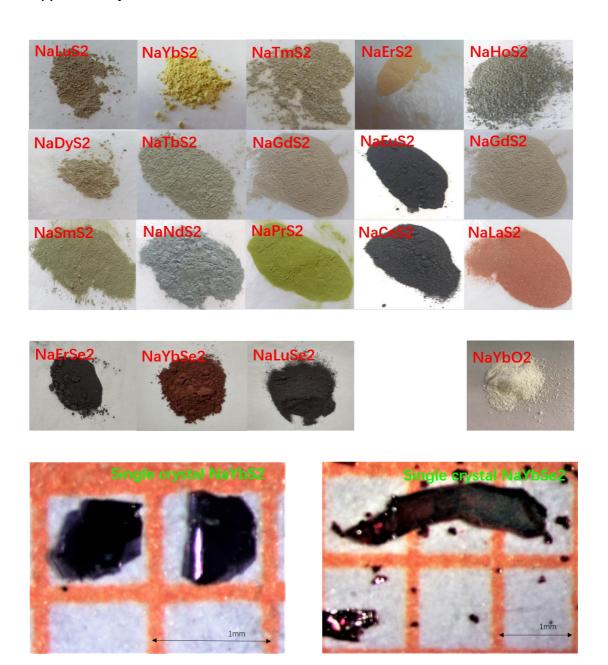


Fig. S1 Photos of NaReCh<sub>2</sub> polycrystals and single crystals (Ch=O, S, Se; Re=La-Lu).

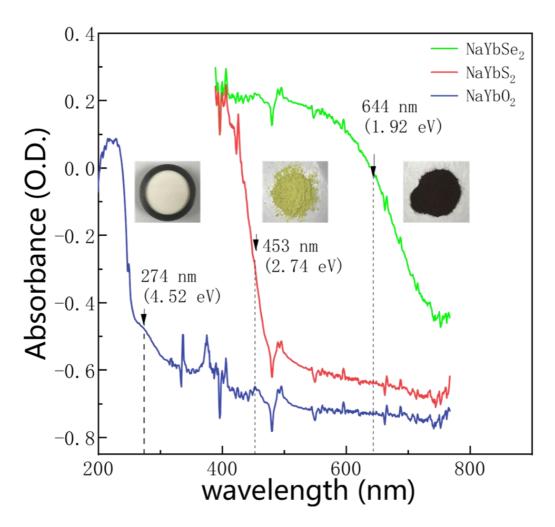


Fig. S2 Absorption spectra of NaYbCh<sub>2</sub> polycrystals (Ch=O, S, Se).

plate1	plate1			Atom p	percent		
		1	2	3	4	5	average
	Na	24.26	24.50	25.20	24.33	25.62	24.782
	Yb	24.18	24.15	22.94	24.11	22.08	23.492
	S	51.56	51.34	51.86	51.56	52.30	51.724
Marie San	Total	100	100	100	100	100	99.998
	Na:Yb:S			1.06:	1:2.2		
Soreta	plate2			Atom p	percent		
rinteX	plate2	1	2	Atom p	percent 4	5	average
	plate2 Na	1 24.20	2 24.37	- 6	<i>h</i>	5 24.51	average
				3	4		
nated and a	Na	24.20	24.37	3 22.77	4 23.95	24.51	23.96
	Na Yb	24.20 24.68	24.37 24.24	3 22.77 23.73	4 23.95 23.93	24.51 24.41	23.96 24.198

Fig. S3 Element ratio analyzed by EDX method

Table S1 Powder diffraction and structural parameters given by Rietveld refinement.

X-ra	y diffraction and	d structural refir	nement for NaYl	oCh2
		(Ch=O, S, Se)		
Compounds		$NaYbO_2$	NaYbS <sub>2</sub>	NaYbSe <sub>2</sub>
Radiation		Cu $K_lpha$	Cu $K_lpha$	Cu $K_{lpha}$
Temperature		300K	300K	300K
Symmetry		R-3m	R-3m	R-3m
Lattice	a = b	3.35113Å	3.90839Å	4.05753Å
constants	С	16.5292Å	19.88553Å	20.7744Å
Cell volume	V	160.7547Å <sup>3</sup>	263.06573Å <sup>3</sup>	296.1973Å <sup>3</sup>
Crystal size	L	443.3nm	800nm	1409.8nm
	G	137.6nm	200nm	3612.0nm
Residuals	Rwp	0.07509	0.04754	0.08207
		Atom sites		
Na <sup>+</sup>	x = y	0	0	0
	Z	0.5	0.5	0.5
Occupancy		1	1	1
Yb <sup>3+</sup>	x = y	0	0	0
	Z	0	0	0
Occupancy		1	1	1
$Ch^{2-}$ (Ch = O, S, Se)	x = y	0	0	0
	Z	0.25744	0.25835	0.25811
Occupancy		1	1	1
	Selecte	ed interatomic d	istance	
Yb-Ch(Ch = O, S, Se)		3.148Å	3.249Å	3.283Å
Yb-Yb		3.35113Å	3.90839Å	4.05753Å
Distance between adjacent Yb3+ layers	d = c/3	5.41973Å	6.62851Å	6.82480Å

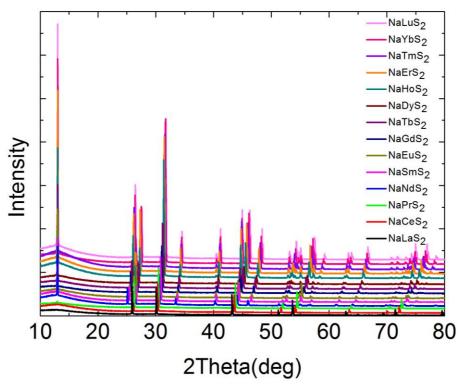


Fig. S4 X-ray diffraction patterns for NaReS $_2$  (Re=La-Lu).

Table S2 Structural parameters of NaReS<sub>2</sub> (Re=La-Lu) extracted from Rietveld refinement.

	Space group	$a \stackrel{0}{(A)}$	$c \left( egin{matrix} 0 \ { m A} \end{array}  ight)$	$V\left(\stackrel{0}{ m A}^3\right)$	$R_{wp}(\%)$
NaLaS <sub>2</sub>	Fm3m	5.88564		203.88318	10.361
$NaCeS_2$	$Fm\overline{3}m$	5.83911		199.08539	3.958
$Na \operatorname{Pr} S_2$	$Fm\overline{3}m$	5.80706		195.82505	7.631
$NaNdS_2$	$R\overline{3}m$	4.10792	19.93425	291.32228	3.873
$NaSmS_2$	$R\overline{3}m$	4.06054	19.91429	284.35656	3.976
$NaEuS_2$	$R\overline{3}m$	4.05160	19.99367	284.23395	5.699
$NaGdS_2$	$R\overline{3}m$	4.02044	19.93933	279.11896	4.079
$NaTbS_2$	$R\overline{3}m$	3.99581	19.91911	275.42901	4.934
$NaDyS_2$	$R\overline{3}m$	3.97570	19.91535	272.61305	3.936
$NaHoS_2$	$R\overline{3}m$	3.95743	19.91548	270.11410	3.733
$NaErS_2$	$R\overline{3}m$	3.94007	19.90959	267.67098	3.926
$NaTmS_2$	$R\overline{3}m$	3.92351	19.89094	265.17629	3.468
$NaYbS_2$	$R\overline{3}m$	3.90839	19.88553	263.42901	4.754
NaLuS <sub>2</sub>	$R\overline{3}m$	3.89552	19.89603	261.47335	4.793

Table S3 Basic parameters of the existing AReO<sub>2</sub> (A=monovalent ions, Re=Rare earth).  $T_{min}$ ,  $\theta_{CW}$  and  $\mu_{eff}$  are the lowest measurement temperature, Curie-Weiss temperature and effective spin moment, respectively.

	0	La	Се	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Υ
Space group		P2 <sub>1</sub> /c	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c	pbnm	pbnm	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c	I4 <sub>1</sub> /amd	I4 <sub>1</sub> /amd	I4,/amd	I4,/amd
$T_{\min}$ / $K$	Li	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
$\theta_{\scriptscriptstyle CW}$ / $K$																
$\mu_{\scriptscriptstyle eff}$				3.56	3.44	1.49	3.35	7.68	9.63	10.03	10.30	9.38	7.45	4.65		
Space group		I4,/amd	I4 <sub>1</sub> /amd	I4,/amd	I4 <sub>1</sub> /amd	I4,/amd	I4 <sub>1</sub> /amd	I4,/amd	C2/c	C2/c	C2/c	C2/c	C2/c	R3m	R3m	R3m
$T_{\min}$ / $K$					1.8	1.8	1.8	1.8		1.8	1.8	1.8	1.8	1.8		
$\theta_{\scriptscriptstyle CW}$ / $K$	Na				2.53			23.4		29.4	- 37.9	- 19.1	- 47.5	- 104		
$\mu_{e\!f\!f}$					3.49	1.59	3.25	7.59		10	10.0	8.75	7.14	4.48		
Space group	K	R3m		R3m	R3m	R3m	R3m	R3m	R3m	R3m	R3m	R3m	R3m	R3m	R3m	R3m
$T_{\min}$ / $K$					1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
$\theta_{\scriptscriptstyle CW}$ / $K$					-80			-11.3	-29.1	-18.6	-608	-12.8	-18.8	-77		

$\mu_{e\!f\!f}$				3.79	1.57	3.49	7.75	9.23	10.33	10.09	9.35	7.00	4.31		
Space group		R3m		R3m	R3m	R3m	R3m		R3m	R3m	R3m	R3m	R3m	R3m	
$T_{\min}$ / $K$	Rb														
$\theta_{\scriptscriptstyle CW}$ / $K$															
$\mu_{\it eff}$															
Space group				P63/mmc											
$T_{\min} / K$	Cs														
$\theta_{\scriptscriptstyle CW}$ / $K$															
$\mu_{\it eff}$															
Space group												R3m	R3m	R3m	
$T_{\min} / K$	Ag											1.8	1.8	1.8	
$\theta_{\scriptscriptstyle CW}$ / $K$												-34	-66		
$\mu_{e\!f\!f}$												7.52	4.46		

Table S4 Basic parameters of the existing AReS<sub>2</sub> (A=monovalent ions, Re=Rare earth).  $T_{min}$ ,  $\theta_{CW}$  and  $\mu_{eff}$  are the lowest measurement temperature, Curie-Weiss temperature and effective spin moment, respectively.

	S	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Υ
Space					Fm3m	Fm3m		Fm3m	Fm3m	R3m	R3m	$R\overline{3}m$				Fm3m
group					111311	177577		111311	177.577	K3m	K3m	K3m				1 11311
$T_{\min}$ / $K$	Li				77	77		77	77	77	77	77				
$\theta_{CW}$ / $K$					-99			-6.2	-8.4	0.7	1.2	-5.5				
$\mu_{e\!f\!f}$					3.32		1.08	7.87	9.77	9.99	9.61	9.42				
Space		Fm3m	Fm3m		Fm3m	Fm3m		R3m	R3m	22	R3m	n=	n=	n=	22	n=
group		Fm5m	Fm5m		Fm5m	Fm5m		R3m	R3m	R3m	R3m	R3m	R3m	R3m	R3m	R3m
$T_{\min} / K$	No		77		77	77		77	77	77	77	77				
$\theta_{\scriptscriptstyle CW}$ / $K$	Na		-		-6.7			2.7	9.4	-5.1	-4.9	1.4				
O <sub>CW</sub> / K			80.7		-0.7			2.1	9.4	-5.1	-4.9	1.4				
$\mu_{e\!f\!f}$			2.21		3.52	1.22		7.49	9.43	10.15	10.30	8.97				
Space					R3m	R3m			R3m	R3m	R3m	$R\overline{3}m$	R3m	R3m		
group					K3m	K3m			K3m	K3m	K3m	K3m	K3m	K3m		
T <sub>min</sub> / K	К															
$\theta_{CW}$ / $K$																
$\mu_{e\!f\!f}$																

Space		R3m	$R\overline{3}m$	$R\overline{3}m$	$R\overline{3}m$	R3m	$R\overline{3}m$	R3m	$R\overline{3}m$	$R\overline{3}m$						
group																
$T_{\min}$ / $K$	Rb															
$\theta_{\scriptscriptstyle CW}$ / $K$																
$\mu_{ m \it eff}$																
Space		$R\overline{3}m$	$R\overline{3}m$	$R\overline{3}m$	$R\overline{3}m$	R3m	$R\overline{3}m$	R3m	$R\overline{3}m$							
group		KSM	Кэт	КЭШ	КЗШ	Кэт	кэт	кэт	кэт	КЗШ	кэт	кэт	КЗШ	Кэт	кэт	
$T_{\min} / K$	Cs															
$\theta_{CW}$ / $K$																
$\mu_{e\!f\!f}$																
Space						P2 <sub>1</sub>		$P2_1$		P2 <sub>1</sub>	P2 <sub>1</sub>	P2 <sub>1</sub>	Fm3m	Fm3m	Fm3m	P2 <sub>1</sub>
group						1 Z <sub>1</sub>		1 21		1 Z <sub>1</sub>	1 Z <sub>1</sub>	1 21	РТЭТ	rmsm	Ртэт	1 Z <sub>1</sub>
$T_{\min} / K$	Ag															
$\theta_{\scriptscriptstyle CW}$ / $K$																
$\mu_{\it eff}$																

Table S5 Basic parameters of the existing AReSe<sub>2</sub> (A=monovalent ions, Re=Rare earth).  $T_{min}$ ,  $\theta_{cw}$  and  $\mu_{eff}$  are the lowest measurement temperature, Curie-Weiss temperature and effective spin moment, respectively.

	Se	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Y
Space group					Fm3m	Fm3m		R3m	R3m	R3m	R3m	$R\overline{3}m$				R3m
$T_{\min}$ / $K$	τ.				77	77		77	77	77	77	77				
$\theta_{\scriptscriptstyle CW}$ / $K$	Li				-20.3			4	-12	7.6	-6.7	-9.1				
$\mu_{ m eff}$					3.54	1.08		7.67	9.78	10.15	10.54	9.39				
Space group		$R\overline{3}m$	R3m		R3m	R3m		R3m	$R\overline{3}m$	R3m	R3m	$R\overline{3}m$		$R\overline{3}m$		R3m
$T_{\min} / K$	NJ.		77		77			77	77	77	77	77				
$\theta_{\scriptscriptstyle CW}$ / $K$	Na		-73.7		-4.4			5.6	-2	-10.7	-1.2	4.1				
$\mu_{e\!f\!f}$			2.3		3.34	1.16		7.61	10.27	10.88	10.54	9.05				
Space group						R3m								$R\overline{3}m$		
T <sub>min</sub> / K	W															
$\theta_{CW}$ / $K$	K															
$\mu_{e\!f\!f}$																
Space group		$R\overline{3}m$	R3m	$R\overline{3}m$	R3m	R3m	$R\overline{3}m$	R3m	$R\overline{3}m$	R3m	R3m	$R\overline{3}m$	R3m	$R\overline{3}m$	R3m	R3m
$T_{\min} / K$	Rb		5						5			5				
$\theta_{\scriptscriptstyle CW}$ / $K$			-113.1						-2.58			-4.8				

$\mu_{e\!f\!f}$		2.68				9.78			9.47				
Space group											P63/mmc		
$T_{\min}$ / $K$	Cs												
$\theta_{\scriptscriptstyle CW}$ / $K$	CS												
$\mu_{\it eff}$													
Space group					I4 <sub>1</sub> /amd	I4,/amd	P2 <sub>1</sub>						
$T_{\min}$ / $K$	Λα												
$\theta_{\scriptscriptstyle CW}$ / $K$	Ag												
$\mu_{e\!f\!f}$													