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

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Frustrated quantum magnets are expected to host many exotic quantum spin states like quantum spin liquid (QSL), and have attracted numerous interest in modern condensed matter physics. The discovery of the triangular lattice spin liquid candidate YbMgGaO$_4$ stimulated an increasing attention on the rare-earth-based frustrated magnets with strong spin-orbit coupling. Here we report the synthesis and characterization of a large family of rare-earth chalcogenides AReCh$_2$ (A = alkali or monovalent ions, Re = rare earth, Ch = O, S, Se). The family compounds share the same structure (R$\bar{3}$m) as YbMgGaO$_4$, and antiferromagnetically coupled rare-earth ions form perfect triangular layers that are well separated along the c-axis. Specific heat and magnetic susceptibility measurements on NaYbO$_2$, NaYbS$_2$ and NaYbSe$_2$ single crystals and polycrystals, reveal no structural or magnetic transition down to 50mK. The family, having the simplest structure and chemical formula among the known QSL candidates, removes the issue on possible exchange disorders in YbMgGaO$_4$. More excitingly, the rich diversity of the family members allows tunable charge gaps, variable exchange coupling, and many other advantages. This makes the family an ideal platform for fundamental research of QSLs and its promising applications.

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Introduction.—The concept of quantum spin liquids (QSLs) was originally proposed by P. W. Anderson theoretically over 40 years ago [1]. It describes a highly entangled quantum state for spin degrees of freedom and was initially constructed with a superposition of spin singlets on the triangular antiferromagnet, so-called resonating-valence-bond state [1]. Later on, the possible connection between QSLs and high-temperature superconductivity was theoretically established through doping a QSL Mott insulator [2]. Although the underlying mechanism for the high-temperature superconductivity has not yet come into a consensus, our understanding of QSLs has greatly improved, both from exactly solvable models [3, 4] and several classification schemes [4, 5]. On the experimental side, various frustrated magnetic materials, particularly the triangular-lattice-based antiferromagnets, were considered to be the most promising systems to realize QSLs [6]. So far, a number of compounds have been reported to host QSLs. Among them, the well-known ones include herbertsmithite and its derived compounds [7–14], and triangular organics [15–19]. The magnetic ions in most of these compounds are 3d transition metal ions Cu^{2+} with $S = 1/2$, which may be crucial to enhance quantum fluctuations.

Quite recently, frustrated materials with magnetic rare-earth ions are proposed to be promising QSL candidates [20]. These include the well-known pyrochlore ice materials [21–30], the kagome magnet [31, 32], and the triangular lattice magnets [33–47]. The local degree of freedom for the rare-earth ions that contain an odd number of 4f electrons (excluding Gd^{3+}), is a Kramers doublet and can be mapped to an effective spin $S = 1/2$ degree of freedom. This effective-spin local moment is protected by time reversal symmetry and the point group symmetry. In many cases the non-Kramers rare-earth ions can be taken as effective spin $S = 1/2$ local moments at low temperatures, though lacking the protection from time reversal symmetry [26, 30, 47–49]. The spin-orbit-entangled nature of the rare-earth local moments often brings highly anisotropic spin models that have never been constructed and studied before [26, 45–49]. Thus, the rare-earth-based magnets play an important role in the exploration of novel spin models and the exotic magnetic states on various lattices. Indeed, QSL behaviors and multipolar phases have been proposed for various rare-earth compounds [21–30, 32, 46, 47].

The recent discovery of the triangular lattice magnet YbMgGaO$_4$ has invoked a further interest in the search of spin liquids with strong spin-orbit coupling [33, 34, 44, 45, 50–54]. The compound has a space group symmetry of R$\bar{3}$m, and the Yb^{3+} ions form a flat and perfect triangular lattice [33, 34] The availability of high-quality single crystals allows extensive and careful studies of magnetic properties using neutron scattering [36–39], muon spin relaxation (muSR) [35], electron spin resonance (ESR) [34] etc. These studies point to a possible gapless U(1) QSL ground state [33–37, 39, 40, 52, 53]. On the other hand, some experiments and theoretical
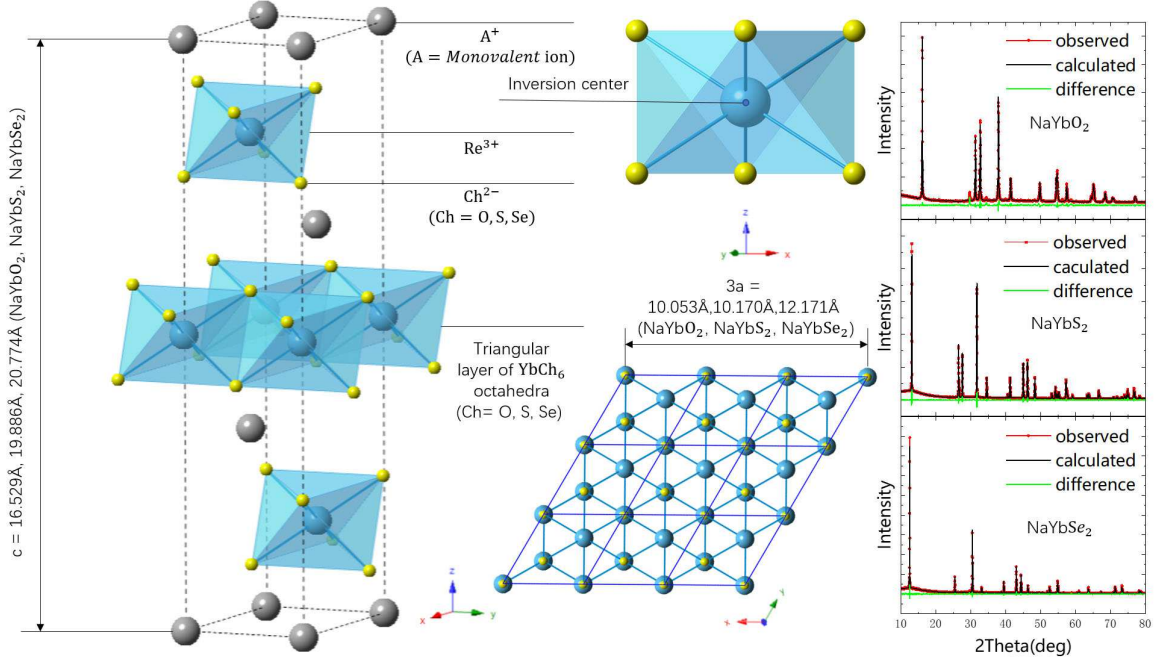
FIG. 1. (Color online.) The general crystal structure of rare-earth chalcogenides and the powder diffraction patterns and Rietveld refinements for NaYbCh$_2$ (Ch = O, S, Se).

arguments raised the issue on Ga/Mg disorder, which was suggested to be responsible for the disordered spin state and/or QSL stability [33, 37, 39, 54–56]. The small exchange coupling allows an easy tunability of the spin state with a laboratory magnetic field [33, 37, 39, 44]. Meanwhile, it also requires that most experiments must be carried out at ultralow temperatures. In some cases this could be an obstacle for in-depth studies and possible applications.

As mentioned above, there is a long list of rare-earth magnets [20, 45, 47]. Then the question is if one can find out some interesting compounds or systems with larger exchange couplings and without disorder. This is the purpose of this work. We systematically synthesized the rare-earth chalcogenides AReCh$_2$ (A = alkali or monovalent ions, Re = rare earth, Ch = O, S, Se) with a delafossite structure. We carried out the structural and thermodynamic characterizations of these compounds. The compounds have a high symmetry of R$\bar{3}$m and perfect spin triangular layers. The magnetic measurements indicate that spins are antiferromagnetically coupled in all the compounds with a range of Curie-Weiss temperatures. For the representative NaYbCh$_2$ (Ch = O, S, Se) samples, no magnetic ordering or transition is observed in the specific heat and susceptibility measurements down to 50mK. Thus, this is a large family of QSL candidates with the simplest structure and chemical for-

mula so far. Its crystal structure naturally removes the issue on Ga/Mg disorder proposed for YbMgGaO$_4$. The diversity of the large family makes it an ideal playground for studying the QSL physics and exploring its promising applications.

Sample preparation and experimental methods.—The polycrystals of NaReO$_2$ (Re = Yb, Lu) were synthesized by the method of solid-state reaction under high temperatures:

$$\mathrm{Na_2CO_3 + Re_2O_3 \rightarrow 2NaReO_2 + O_2} \quad \mathrm{(Re=Yb,\ Lu).} \quad (1)$$
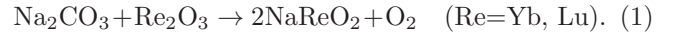
Na$_2$CO$_3$ and Re$_2$O$_3$ powders were mixed in a dry process (mixing molar ratio: Na$_2$O : Yb$_2$O$_3$ = 2.5 : 1) and shaped into a pellet by isostatic pressing (50MPa, 2min). Shaped samples were heated at 900 degrees for 9 hours. After the heating, the samples were ground and washed with distilled water and ethanol, at lastly dried in air at room temperature for 48 hours. The polycrystals of NaReS$_2$ (Re = 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:

$$\mathrm{Na_2S + 2Re + 3S \rightarrow 2NaReS_2,} \quad (2)$$

where Re = Lu, Se, Tm, Er, Ho, Dy, Tb, Gd, Eu, Sm, Nd, Pr, Ce, La. The Na$_2$S, Re and S powder was mixed in Ar environment glove box. The mixed powders were placed in a graphite crucible and vacuum packaged with quartz
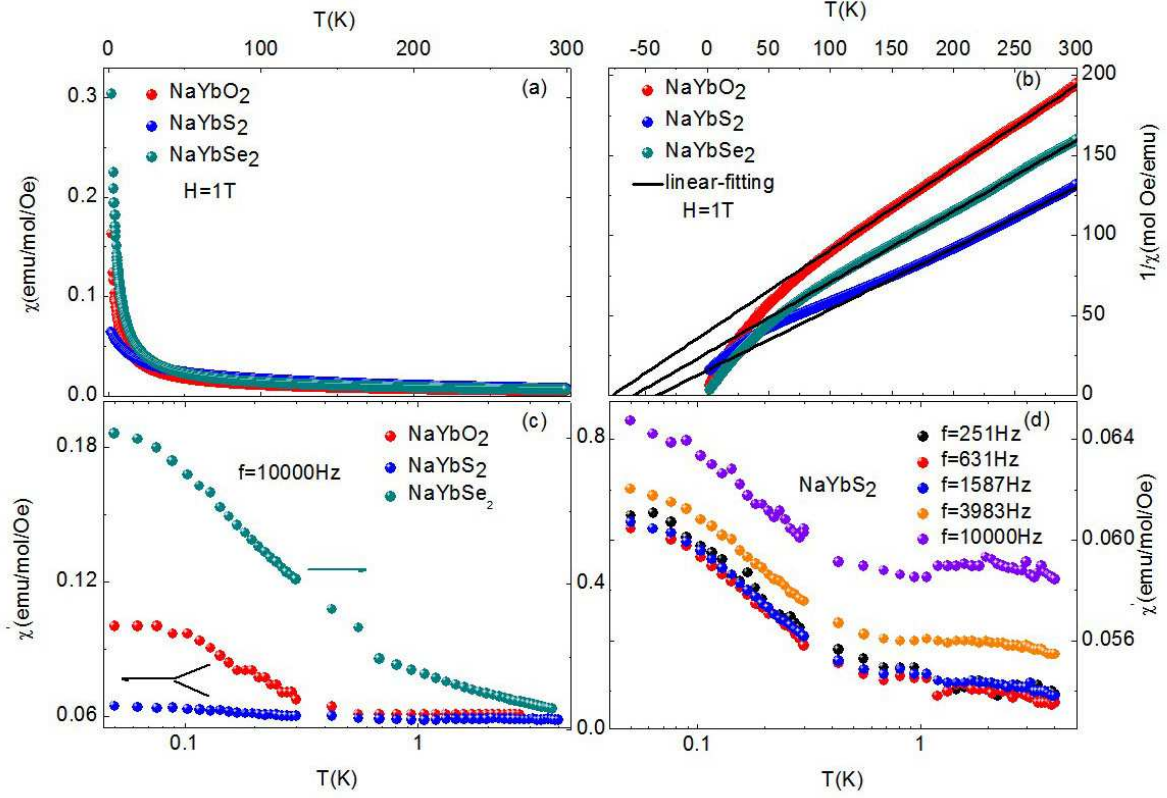
FIG. 2. (Color online.) The DC (a & b) and AC (c & d) magnetic susceptibilities of polycrystalline $NaYbCh_2$ (Ch = O, S, Se).

tube. Packaged samples were heated at 850 degrees for 48 hours. After the heating, the sample were powder and washed with distilled water and then dried in air at 50 degrees for 6 hours. The synthesis of polycrystals of $NaReSe_2$ (Re = Er, Yb, Lu) were similar with the synthesis of powders of $NaReS_2$. The temperature was adjusted to 900 degrees.

We have also successfully grown high quality $NaYbSe_2$ single crystals. The growth conditions of single crystals are more rigorous than $NaYbSe_2$ polycrystals. Na_2Se, Yb and Se powders were mixed in Ar environment glove box (mixing molar ratio: Na_2Se : 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 degrees for 48 hours. After the heating, we can observe 2-3mm size single crystals. We made a simple resistance check for the crystals and the resistance is overranged and thus $NaYbSe_2$ is confirmed to be a good insulator.

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

Ch	Space group	C	Θ_{CW}/K	μ_{eff} (μ_B)
O	R$\bar{3}$m	1.9448	-77.35	3.94
S	R$\bar{3}$m	2.6166	-40.98	4.57
Se	R$\bar{3}$m	2.2550	-59.84	4.24

TABLE I. Parameters extracted from Curie-Weiss fitting for $NaYbCh_2$ (Ch= O, S, Se).

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 a better thermal contact.

Results and discussions.—In Fig. 1, we depict the crystal structure of the rare-earth chalcogenides and the Rietveld refinements for three representative samples $NaYbO_2$, $NaYbS_2$ and $NaYbSe_2$, where the detailed structural information extracted from the refinements can be found in the Supplementary Materials. The system has an R$\bar{3}$m space group symmetry, and

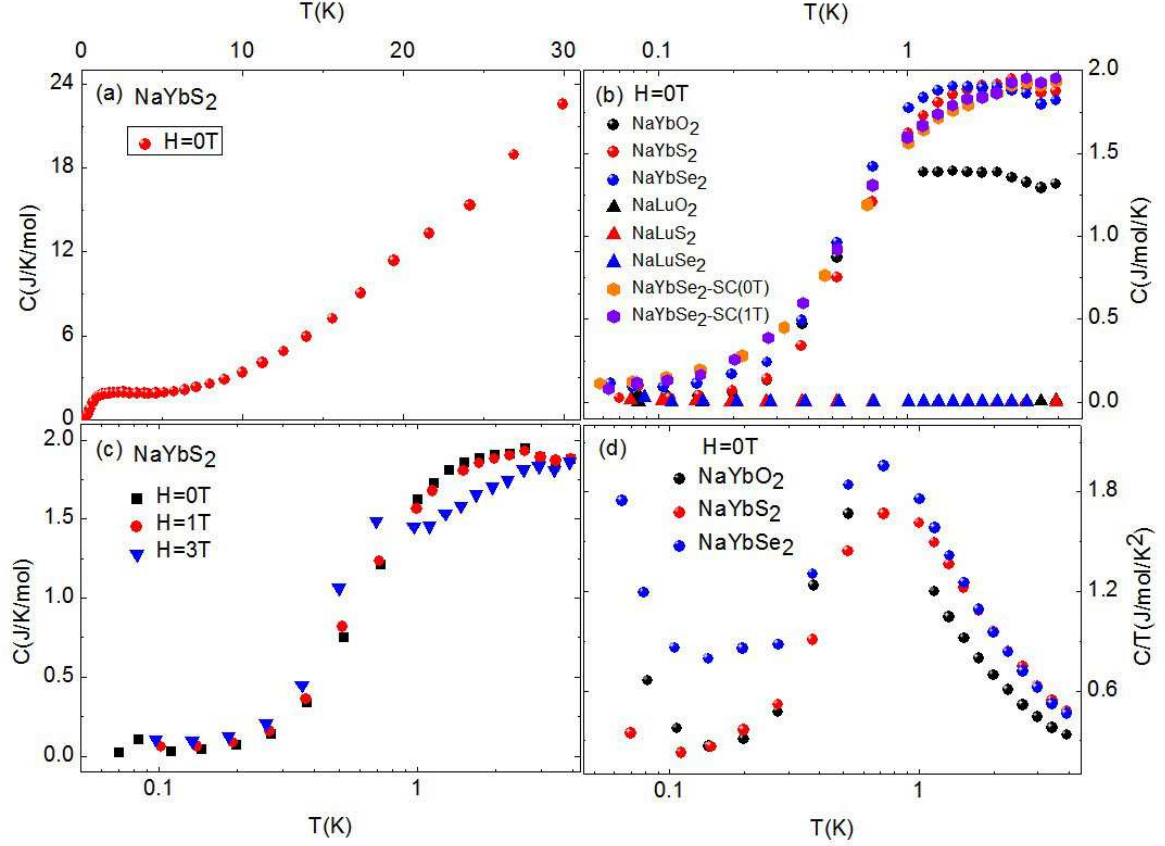FIG. 3. (Color online.) Specific heat measurements on $NaYbCh_2$ (Ch = O, S, Se). Single crystal (SC) $NaYbSe_2$ and polycrystalline $NaYbO_2$ and $NaYbS_2$ were used in the measurements.

the magnetic ions form flat triangular layers that are well separated. The $ReCh_6$ octahedra are connected in an edge-sharing fashion. The local crystal-field environment around the magnetic ions is exactly analogous to the case of $YbMgGaO_4$. Therefore, one expects a similar crystal-field splitting scheme of the Yb^{3+} ions as the one in $YbMgGaO_4$. This means that a spin-orbital-entangled effective spin $S = 1/2$ local moment should hold for our case. Similar to $YbMgGaO_4$, the antisymmetric Dzyaloshinskii-Moriya interaction is prohibited by the inversion symmetry of the system.

The Mg/Ga disorder in the non-magnetic layers of $YbMgGaO4$ has been extensively discussed and is still under debate. Whether or how much this non-magnetic disorder impacts on the Yb magnetic properties is unclear in this stage. In some experiments and theoretical calculations, the disorder was considered to play a dominant role in contributing to the low-energy excitations. As a comparison, there is no such disorder in this family of rare-earth chalcogenides, due to the structural simplicity. The issue on disorder is completely removed for this family of materials. 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 still concerns about the active monovalent ions like Na^+ and K^+, he will have plenty of choices of the heavy monovalent ones such as Rb^+, Cs^+, Cu^+ and Ag^+, etc.

For the selected sub-family $NaYbCh_2$ (Ch = O, S, Se), we measured the DC magnetic susceptibility in the range of 2-300K and the AC susceptibility from 50mK to 4K. The results are presented in Fig. 2. The Curie-Weiss fitting was made from 150K to 300K according to the crystal-field splitting in $YbMgGaO_4$ and the fitting results are summarized in Table. I. Considering the small interaction energy scale of rare-earth moments, this fitting range may not be quite sufficient to characterize the low-energy magnetic physics of the system. A lower fitting range may be required in the future. Nevertheless, the negative Curie-Weiss temperatures suggest an antiferromagnetic coupling in all the samples. Excitingly, the Curie-Weiss temperatures are much larger than that of $YbMgGaO_4$ because of the smaller distances between nearest-neighbor Yb^{3+} in the rare-earth chalcogenides. The AC susceptibility for the three samples shows no sign of long-range magnetic ordering. The measurements under various frequencies further confirms that there is no spin freezing either. Interestingly, the susceptibility sat-
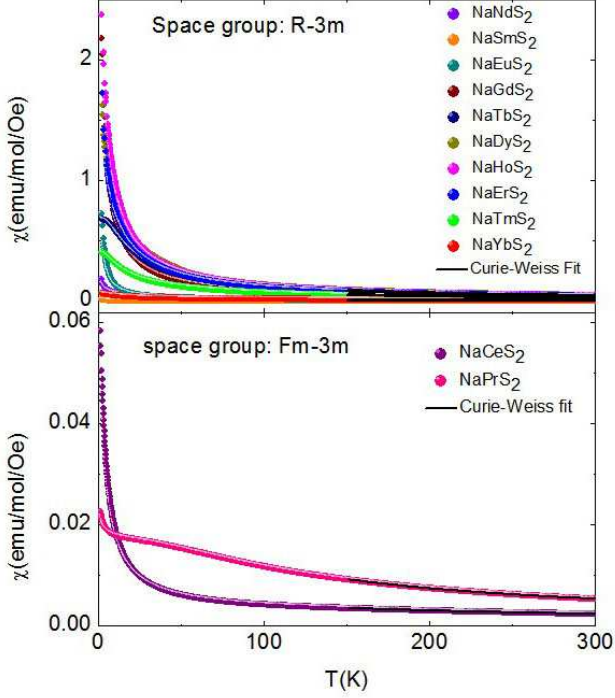
FIG. 4. (Color online.) Magnetic susceptibility of NaReS$_2$ (Re = Ce-Yb) in the range of 2K to 300K.

uration in the zero temperature limit is clearly observed for all the three samples. This should be one of the consequences caused by strong spin-orbit coupling rather than a sign of finite density of spin excitations. Under the strong spin-orbit coupling, the total magnetization is not a good quantum number and cannot be used to label the many-body eigenstate. The many-body eigenstate would be a mixture of states with different total magnetizations. The magnetic susceptibility would always be a constant. We also find that the low-temperature susceptibility of NaYbSe$_2$ is obviously larger than that of the other two compounds. In fact, the distance between nearest neighbor Yb^{3+} ions in NaYbSe$_2$ is larger, while its Curie-Weiss temperatures and the moment obtained from the Curie-Weiss fitting look comparable to the other two.

Our specific heat results are shown in Fig. 3. There is no obvious transition down to 50mK in these compounds, and it is consistent with the conclusion from the magnetic susceptibility data. We observed no apparent change or shift with applying a magnetic field up to 3T (see Fig. 3c). On the other hand, an upturn is observed below 100mK in the C/T-T plot (see Fig. 3d). This may arise from the nuclear Schottky anomaly due to the nuclear spins. The upturn makes it difficult to obtain the intrinsic trend of the specific heat below 100mK and to conclude whether the system is a gapless or gapped QSL. Thus, more detailed magnetic and thermodynamic exper-

iments are required in the future. The broad peak around 1K in the C/T-T plot is considered to be a consequence of preserving entropy. Here we point out that there is no obvious disorder in the present case and we still do not observe any long-range magnetic ordering or freezing that points to a possible QSL ground state. This means that the rare-earth triangular system, including rare-earth chalcogenides reported here and YbMgGaO$_4$, intrinsically hosts the QSL state that is not stabilized by or even originated from the Ga/Mg charge disorder.

The measurements discussed above are based on the sub-family NaYbCh$_2$ (Ch = O, S, Se). Towards a comprehensive view of the large family, we fixed Na and S, and systematically synthesized the other sub-family NaReS$_2$ (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 preserve the high lattice symmetry of R$\bar{3}$m. But the three end members, NaLaS$_2$, NaCeS$_2$ and NaPrS$_2$ show a cubic structure with the space group symmetry of Fm$\bar{3}$m. Clearly this is caused by the larger ionic radii of La, Ce and Pr. The magnetic susceptibility measurements from 2K to 300K have been carried out on the sub-family and the results are presented in Fig. 4. No obvious magnetic transition is observed in all the compounds with the R$\bar{3}$m symmetry. Similar to the R$\bar{3}$m brothers, the cubic NaCeS$_2$ also shows no sign of magnetic transition from 2K to 300K, as the perfect triangular lattice formed by the magnetic ions remains undistorted and the strong geometrical frustration is always there. In contrast, an anomaly appears around 10K in the susceptibility of NaPrS$_2$ (Fm$\bar{3}$m).

The Curie-Weiss fitting was performed from 150K to 300K, assuming a reasonably high crystal field splitting. The full results are presented in Table II. We can see that the exchange couplings vary from sample to sample. In the 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 4.5eV, 2.7eV and 1.9eV for NaYbO$_2$, NaYbS$_2$, and NaYbSe$_2$, respectively. The variable and small charge gaps may allow the system to access a Mott-metal transition by applying doping or pressures. Such a possibility opens up the interesting direction of Mott transitions out of a QSL [57]. This transition was argued to be continuous by noticing that the Landau damping term scales like a mass term for the bosonic charge and then identifying the transition as an usual superfluid-Mott transition [57]. Thus, 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$\bar{3}$m and hence are potential QSL materials (see Supple-

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

TABLE II. Parameters extracted from the Curie-Weiss fitting for $NaReS_2$ (Re = Ce-Yb).

mentary Materials). This suggests that the family is an ideal playground, on which we can tune the basic material parameters or exchange coupling to explore the QSL physics and develop its possible applications.

Summary.—In summary, we have synthesized rare-earth chalcogenides $AReCh_2$ that exhibit a delafossite structure, and made structural and thermodynamics characterizations. The family has a lattice symmetry R$\bar{3}m$, and the magnetic ions are antiferromagnetically coupled and form perfect triangular layers. The magnetic susceptibility and specific heat measurements down to 50mK indicate no sign of long-range magnetic ordering or transition. The family removes the disorder issue raised in $YbMgGaO_4$ and also suggests the QSL physics is probably not from disorder. The unique advantages, such as various charge gaps and exchange coupling, suggest that the family may be an ideal platform for the further study of QSLs.

Note added: Upon the completion of this work, we become aware of Ref. 58 that focused on $NaYbS_2$ and proposed it as a spin liquid candidate.

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