Crystal-electric-field excitations in a quantum-spin-liquid candidate NaErS$_2$

Shang Gao,$^{1,}$† Fan Xiao,$^{2,3,}$† Kazuya Kamazawa,$^4$ Kazuhiko Ikeuchi,$^4$ Daniel Biner,$^3$ Karl W. Krämer,$^3$ Christian Rüegg,$^{5,6}$ and Taka-hisa Arima$^{1,7}$

$^1$RIKEN Center for Emergent Matter Science, Wako 351-0198, Japan
$^2$Laboratory for Neutron Scattering and Imaging, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
$^3$Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, Bern, Switzerland
$^4$Neutron Science and Technology Center, Comprehensive Research Organization for Science and Society, Tokai, Ibaraki, 319-1106, Japan
$^5$Research Division Neutrons and Muons, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
$^6$Department of Quantum Matter Physics, University of Geneva, CH-1211 Geneva, Switzerland
$^7$Department of Advanced Materials Science, University of Tokyo, Kashiwa 277-8561, Japan

(Dated: November 26, 2019)

The delafossite family of compounds with a triangular lattice of rare earth ions has been recently proposed as a candidate host for quantum spin liquid (QSL) states. To realize QSLs, the crystal-electric-field (CEF) ground state of the rare earth ions should be composed of a doublet that allows sizable quantum tunneling, but till now the knowledge on CEF states in the delafossite compounds is still limited. Here we employ inelastic neutron scattering (INS) to study the CEF transitions in a powder sample of the delafossite NaErS$_2$, where the large total angular momentum $J = 15/2$ of the Er$^{3+}$ ions and the resulting plethora of CEF transitions enable an accurate fit of the CEF parameters. Our study reveals nearly isotropic spins with large $J_x = \pm 1/2$ components for the Er$^{3+}$ CEF ground states, which might facilitate the development of a QSL state. The scaling of the obtained CEF Hamiltonian to different rare earth ions suggests that sizable $J_z = \pm 1/2$ components are generally present in the CEF ground states, supporting the ternary sulfide delafossites as potential QSL hosts.

I. INTRODUCTION

The QSL state, where the conventional magnetic long-range order (LRO) is completely removed by quantum fluctuations, has been fascinating physicists since it was proposed in the 1970s (Ref. 1). Similar to the well-known cases of one-dimensional spin chains, the fundamental excitations in QSLs are fractional spin-1/2 excitations called spinons, which can be either gapped or gapless depending on the specific system. Theoretical investigations have revealed the spinons in some QSLs to be highly entangled with each other, leading to fractional statistics and exotic braiding properties that might be utilized for topological quantum computing.

The initial quest for QSLs was focused on intrinsically spin-1/2 systems such as the Cu$^{2+}$-based compounds. One prominent example is the herbertsmithite ZnCu$_3$(OH)$_6$Cl$_2$ (Ref. 10–12). In this compound, the Cu$^{2+}$ ions form a two-dimensional (2D) kagomé lattice with geometric frustration. Using INS, an almost featureless excitation continuum was revealed, which is consistent with the spinon excitations and, more importantly, demonstrates that QSL can exist in real materials.

Recently, the search for QSL candidates has been extended to the rare earth systems. This is surprising at the first glance, because the rare earth ions usually have a relatively large angular momentum $J$, which disfavors quantum fluctuations. However, with an appropriate CEF, the ground state doublet of the rare earth ions might have considerable components of $|J, J_z\rangle$ with a relatively small $|J_z|$ that allows quantum tunnelling. If this ground state is well separated from the excited states, the spin degree-of-freedom of the rare-earth ions will effectively behave as spin-1/2. One of the best-known examples is the quantum spin ice state realized in the rare-earth pyrochlores. For the Dy and Ho-based pyrochlore systems with only relatively large $|J_z|$ components in the CEF ground state, a classical spin ice state is realized, where each tetrahedron has a two-in-two-out spin configuration. While for the Tb, Yb, and Pr-based pyrochlores, a relatively high magnitude of quantum spin tunnellings is observed, which drives the classical spin ice state into a QSL state with emergent U(1) quantum electrodynamics.

Given the success of the effective spin-1/2 picture in the rare-earth pyrochlores, it is natural and tempting to advance this concept to other frustrated lattices, especially the 2D triangular lattice where the idea of QSL was originally conceived. According to theoretical calculations, the effective spin-1/2 Hamiltonian for rare earth spins on a triangular lattice might contain transverse coupling terms that can induce competing ground states in the classical solution, whereupon a QSL state could emerge near the phase boundary once quantum fluctuations are included. Following this argument, the triangular lattice compound YbMgGaO$_4$ has recently been proposed as a candidate host for the QSL state. However, due to the Mg-Ga disorder that is intrinsic in this compound, it is unclear whether the broad excitations that have been observed in INS are due to quantum fluctuations or disorder effects.

The delafossite family of compounds ALaX$_2$, where La are rare earth ions, A = Na, K, Cu(I), and X = O,
ment. As exemplified by the spin ice compounds it is crucial to have an overview of their CEF environments in both compounds and suggested similar to different rare earth ions will foster the search for QSL states in the sulfide delafossites.

\[ J_{\text{spins}} \approx \frac{7}{3} \text{ components for the Er}^{3+} \text{ ions with a larger } J \text{ allow more CEF transitions, which will enable a more accurate fit of the CEF parameters and thus provide a reference in the study of the similar delafossite compounds.} \]

Here we report INS investigations on the CEF transitions in NaErS\(_2\), where the Er\(^{3+}\) has a total angular momentum of \( J = 15/2 \). Our studies reveal nearly isotropic spins with large \( J_z = \pm 1/2 \) components for the Er\(^{3+}\) CEF ground state doublet that allow spin quantum tunnelling\(^{13,14} \). The scaling of the obtained CEF Hamiltonian to different rare earth ions will foster the search for QSL states in the sulfide delafossites.

II. EXPERIMENTAL DETAILS

Polycrystalline samples of NaErS\(_2\) were prepared using the solid state method proposed by Schleid \textit{et al.} \(^{30} \), in which NaCl served as both reagent and flux. Under N\(_2\), Er grains, sulfur, and NaCl in a molar ratio of 2:3:9 were loaded into a Ta ampoule, which was sealed by arc-welding under He. The Ta ampoule was sealed in a silica ampoule under vacuum, slowly heated up to 850°C with \( 20°C/h \) and kept for 7 days before cooling down to room temperature. The final product was rinsed with H\(_2\)O and acetone several times to remove water-soluble Na\(_3\)ErCl\(_6\).

Powder x-ray diffraction (XRD) patterns were measured on a STOE STADIP diffractometer in reflection (Bragg-Brentano) geometry in air at room temperature. Diffraction patterns with Cu K\(_{\alpha1}\) radiation (\( \lambda = 1.54059 \) Å) from a focusing α-SiO\(_2\) (101) monochromator were recorded on a linear position-sensitive detector with 0.01° resolution in 2θ. Rietveld refinement was performed in the \( R3m \) space group using the FULLPROF program\(^{44} \).

INS experiments were performed on the 4SEASONS time-of-flight (TOF) spectrometer at the Materials and Life Science Experimental Facility MLF of J-PARC in Japan\(^{45} \). The setup with a radial collimator and a neutron beam size of 20 × 20 mm\(^2\) was employed. A NaErS\(_2\) powder sample of 1.8 g was packed in an envelope of aluminum foil, curled up and installed in an aluminum sample can with outer/inner diameter of 20.5/20.0 mm. This configuration reduced the neutron absorption caused by the Er isotopes in the sample\(^{42,46} \). For our measurements, the chopper frequency was set to 300 Hz, and the repetition rate multiplication method\(^{47} \) allows the measurement with multiple incident energies of \( E_i = 222, 80, 41, 24.7, 16, \) and 12 meV to be collected at the same time. A GM refrigerator was mounted to reach temperatures between 5 and 250 K. Besides the NaErS\(_2\) sample, measurements were also performed on a vanadium standard to allow a quantitative comparison for data collected at 300 K with the same instrumental setup. The acquired data were analyzed with the UTSUSEMI software package\(^{48} \).
E_i = 16 \text{ meV}, T = 5 \text{ K} \\
E_i = 16 \text{ meV}, T = 50 \text{ K} \\
E_i = 41 \text{ meV}, T = 5 \text{ K} \\
E_i = 41 \text{ meV}, T = 50 \text{ K}

(a) 

(b) 

(c) 

(d) 

FIG. 3. INS spectra $S(Q, \omega)$ of a NaErS$_2$ powder sample collected on 4SEASONS at temperatures $T = 5 \text{ K}$ (panels a and b) and 50 $\text{ K}$ (panels c and d), with incoming neutron energy $E_i = 16 \text{ meV}$ (panels b and d) and 41 $\text{ meV}$ (panels a and c). At elevated temperatures, additional excitations originating from thermally populated doublets are observed.

III. RESULTS

The XRD pattern for our NaErS$_2$ sample is shown in Fig. 2. The refined lattice parameters $a = 3.9342(1)$ Å and $c = 19.8421(2)$ Å are in good agreement with the published crystal structure$^{30}$. NaErS$_2$ crystallizes in space group $R3m$ with Na$^{+}$ and Er$^{3+}$ ions on sites 3$b$ (0 0 0.5) and 3$a$ (0 0 0), respectively. The $S^2^−$ ions occupy the site 6$c$ (0 0 $z$) with $z = 0.2573(3)$. A satisfactory fit was obtained by including a preferred orientation along the [001] direction due to the plate-like habit of the NaErS$_2$ polycrystals. The $R$-factors are $R_p = 18.7 \%$, $R_{wp} = 20.9 \%$, and $\chi^2 = 2.2$. Introducing site vacancies or anti-site disorders does not improve the $R$-factors.

A secondary phase is observed in all the synthesized batches, which can be assigned to Er$_{2+x}$S$_{3+y}$ impurities and has been treated with the Le Bail profile fit assuming a $P2_1/m$ space group. Using the strongest reflections for NaErS$_2$ at $2\theta \sim 13^\circ$ (not included in the refinement due to the underestimation of intensities at low-angles in the reflection geometry) and for the secondary phase at $2\theta \sim 25^\circ$, the fraction of the secondary phase is estimated to be $\sim 5\%$.

The contour plots in Fig. 3 summarize the NaErS$_2$ neutron spectra collected at $T = 5$ and 50 $\text{ K}$ with $E_i = 16$ and 41 $\text{ meV}$. The strong intensity spot in the $E_i = 41 \text{ meV}$ spectra at wavevector transfer $Q = 5.5 \text{ Å}^{-1}$ and energy transfer $E = 34 \text{ meV}$ is spurious due to unshielded scattered neutrons from the beam catcher. For TOF neutron spectrometers, the energy resolution scales with the incoming neutron energy and can be estimated by the full-width-half-maximum (FWHM) of the incoherent scattering in the vanadium standard measurements. In our experiment, the energy resolution was estimated to be 0.50, 0.80, and 2.51 meV for $E_i = 12$, 16, and 41 meV, respectively. Therefore, a relatively high $E_i$ of 41 meV allow access to the high energy excitations, while a relatively low $E_i$ of 16 or 12 meV resolves the different excitations at low energies.

At $T = 5 \text{ K}$, four dispersionless excitations are observed at around 2.0, 4.0, 6.0, and 6.8 $\text{ meV}$ in the $E_i = 16 \text{ meV}$ spectra shown in Fig. 3b, and three relatively weak excitations can be discerned at 26.5, 28.3, 30.9 $\text{ meV}$ in the $E_i = 41 \text{ meV}$ spectra shown in Fig. 3a. In $D_{3d}$ symmetry, the Er$^{3+}$ $4I_{15/2}$ manifold splits into eight Kramers doublets. Therefore, the seven excitations observed in our INS spectra can be ascribed to the Stokes transitions from the CEF ground state doublet to the seven excited doublets. At an elevated temperature of 50 $\text{ K}$, the excited doublets are thermally populated, leading to two additional transitions at $\sim 2.9$ and 5.0 $\text{ meV}$ in Fig. 3d and three high-energy transitions at 22.0, 24.0, and 26.5 $\text{ meV}$ in Fig. 3c. Transitions at $\sim 2.9, 22.0, 24.0,$ and
D form factor. CEF transitions should be proportional to the magnetic
saturation factors for the CEF operators \( \hat{S} \) usually written as
\[
\sum_{Q} \frac{p_i}{k_i} |\langle f | \hat{j}_i | i \rangle|^2 \delta(E_i - E_f + E),
\]
where \( c \) is a constant, \( |i \rangle \) and \( |f \rangle \) are the eigenfunctions of the CEF Hamiltonian and represent the initial and final wavefunctions, respectively. \( E_i (k_i) \) and \( E_f (k_f) \) are the energies (wavevectors) of the incoming and scattered neutrons, respectively. The occupation probability \( p_i \) for the state at \( E_i \) is described by the Boltzmann distribution
\[
p_i = \exp \left(-E_i/kT\right) / \sum_i \exp \left(-E_i/kT\right). \]
\( J_\alpha \) with \( \alpha = x, y, \) and \( z \) are the angular momentum operators. \( \delta(E_i - E_f + E) \) is the delta function.

Using the simulated annealing scheme implemented in McPhase\(^{50} \), we can fit the INS spectra by varying the CEF parameters. Fig. 5 plots the energy dependence of the INS intensities integrated within a momentum transfer of \( 1.2 - 2.2 (2.2 - 3.2) \) Å\(^{-1} \) for the \( E_i = 12 (41) \) meV data measured at \( T = 5 \) and 50 K, respectively. The calculated spectra are convoluted by a Gaussian function to account for the instrument resolution. Due to the relatively higher intensities and clearer three-peak profile at high energies shown in Fig. 5d, our fit was mainly performed with the data collected at 50 K. The best fit is achieved with the set of CEF parameters shown in Table I. The slight mismatch for the 5 K data at \( E_i \approx 26 \) meV shown in Fig. 5b might be due to the background or impurity scattering.

The obtained CEF ground state wavefunctions for the \( \text{Er}^{3+} \) ions are
\[
|\pm\rangle = \pm 0.115|\pm 11/2\rangle + 0.366|\pm 5/2\rangle + 0.597|\pm 1/2\rangle - 0.507|\pm 7/2\rangle + 0.489|\pm 13/2\rangle. \]
\( g_{||} = 7.44 \) in the \( xy \) plane and \( g_{\perp} = 5.34 \) along the \( z \) direction, which sharply contrasts the Ising anisotropy observed in \( \text{CdEr}_2X_4 \) (\( X = \text{S, Se}\))\(^{42} \). Such a difference originates from the different components of the CEF ground states: in \( \text{CdEr}_2X_4 \) (\( X = \text{S}, \)

\[
\begin{array}{cccccc}
L_2^0 & L_4^1 & L_4^1 & L_6^0 & L_6^0 & L_6^0 \\
24.9(1) & -79.2(4) & -127.2(7) & 30.9(1) & -1.13(1) & 22.2(1)
\end{array}
\]

TABLE I. Fitted Wybourne CEF parameters (meV) for \( \text{Er}^{3+} \) in \( \text{NaErS}_2 \). Errors are conservative estimates based on repeated Monte Carlo simulations.
Se), the ground states are dominated by the $|\pm 15/2\rangle$ components, while in NaErS$_2$, the main components are $|\pm 1/2\rangle$. In the latter case, substantial quantum tunnelling can be expected, which will facilitate the development of the QSL state.

IV. DISCUSSIONS

The fitted CEF parameters and the composition of the Er$^{3+}$ ground state in NaErS$_2$ are very different from the results of the point-charge calculation. Assuming point charges of $2e^-$ on the surrounding sulfur anion sites, the CEF ground state doublet can be calculated to be $|\pm\rangle = 0.984 |\pm 15/2\rangle \pm 0.178 |\pm 9/2\rangle + 0.035 |\pm 3/2\rangle \mp 0.005 |\mp 3/2\rangle$, which is dominated by the $J_z = \pm 15/2$ components and thus results in an Ising spin with $g_{\perp} = 0$ and $g_{\parallel} = 17.76$. The failure of the point charge calculation indicates the importance of further charges beyond the anion octahedra and also the charge distributions due to the covalent character of the Er-S bonds.

The inaccuracy of the point charge calculation is also evident in the Yb-based YbMgGaO$_4$. Considering only the nearest O$^{2-}$ octahedron, the point charge calculation produces a ground state dominated by the the maximal $|J_z\rangle$ components of $|7/2, \pm 7/2\rangle$ and $g$ factors of $g_{\perp} = 0.25$ and $g_{\parallel} = 8.24$, which is again in sharp contrast with the Heisenberg spin fitted from the INS spectra$^{53}$.

The CEF parameters determined for Er$^{3+}$ in NaErS$_2$ can be scaled to other rare earth ions, thus providing basic knowledge on the CEF ground state in the sulfide delafossites. For this purpose, we first calculated the Hutchings CEF parameters for the Er$^{3+}$ ions$^{49}$. The Hutchings CEF parameters depend only on the CEF environment and can be conveniently applied for systems with similar crystal structures$^{31,42}$. Assuming the same Hutchings CEF parameters, Table II lists the corresponding Wybourne CEF parameters for different rare earth ions. Ce$^{3+}$ and Pr$^{3+}$ are omitted because the corresponding NaLnS$_2$ compounds do not crystallize in the $R3m$ space group$^{31}$. For the Kramers ions, the CEF ground state doublet can be calculated as follows:

\begin{align*}
\text{Nd}^{3+} \quad & (J = 9/2) |\pm\rangle = 0.293|\pm 7/2\rangle \pm 0.144 |\pm 1/2\rangle + 0.945 |\mp 5/2\rangle, \\
\text{Sm}^{3+} \quad & (J = 5/2) |\pm\rangle = 0.807|\pm 5/2\rangle \pm 0.591 |\mp 1/2\rangle, \\
\text{Dy}^{3+} \quad & (J = 15/2) |\pm\rangle = 0.313|\pm 13/2\rangle \mp 0.493 |\pm 7/2\rangle + 0.327 |\pm 1/2\rangle \pm 0.536 |\pm 5/2\rangle + 0.515 |\mp 11/2\rangle, \\
\text{Yb}^{3+} \quad & (J = 7/2) |\pm\rangle = 0.471|\pm 7/2\rangle \mp 0.520 |\pm 1/2\rangle - 0.712 |\mp 5/2\rangle. \tag{3}
\end{align*}

Sizable $J_z = \pm 1/2$ components in the ground state doublet are predicted for all the Kramers ions, which supports the delafossites as candidate compounds for QSL states. Especially, in the case of Yb$^{3+}$, the scaled CEF parameters predict three excitations from the CEF ground state at 21.0, 30.0, and 55.8 meV with a cross section of 5.03, 4.02, and 0.09 barn, respectively. This calculation result is close to the experimental observation of two CEF transitions at 23 and 39 meV (Ref. 35). Although the exact crystallographic structure and consequently the Hutchings CEF parameters depend on the rare earth ions, we expect the scaled CEF ground state wavefunction to be qualitatively correct$^{31,42}$, which supports the ternary sulfide delafossites as candidate compounds to realize the QSL state.

V. CONCLUSIONS

INS experiments have been performed on the QSL candidate NaErS$_2$ to study the Er$^{3+}$ CEF transitions. The

| $L_2$ | $L_4$ | $L_6$ | $L_8$ | $L_{10}$ | $L_{12}$ |
|------|------|------|------|------|------|
| Nd$^{3+}$ | -39.0 | -181.6 | -291.6 | 96.4 | -3.5 | 69.4 |
| Sm$^{3+}$ | -34.1 | -141.0 | -226.5 | 0 | 0 | 0 |
| Tb$^{3+}$ | -28.8 | -103.0 | -165.4 | 43.9 | -1.6 | 31.6 |
| Dy$^{3+}$ | -27.3 | -93.9 | -150.8 | 38.7 | -1.4 | 27.9 |
| Ho$^{3+}$ | -26.0 | -86.0 | -138.2 | 34.5 | -1.2 | 24.8 |
| Tm$^{3+}$ | -23.8 | -73.2 | -117.6 | 27.8 | -1.0 | 20.0 |
| Yb$^{3+}$ | -22.8 | -67.9 | -109.1 | 25.2 | -0.9 | 18.1 |

TABLE II. The Wybourne CEF parameters (meV) for different rare earth ions.
measured INS spectra can be fitted with the CEF Hamiltonian, which reveals the existence of large $J_z = \pm 1/2$ components in the ground state doublet that allows quantum fluctuations. Applying the fitted CEF parameters to other rare earth ions reveals that the $J_z = \pm 1/2$ components also exist in the CEF ground states, supporting the rare-earth-based sulfide delafossites as candidate hosts for the QSL state.

VI. ACKNOWLEDGEMENTS

We thank T. Nakajima, M. Soda, L. Ding, and V. Koch for helpful discussions. Our inelastic neutron scattering experiment was performed at the Materials and Life Science Experimental Facility (MLF) of the Japan Proton Accelerator Research Complex (J-PARC) under the user program (Proposal No. 2019A0293). F.X. acknowledges the funding from the European Union’s Horizon 2020 research and innovation program under the Marie Sklodowska-Curie grant agreement No 701647.
39. L. Ding, P. Manuel, S. Bachus, F. Grußler, P. Gegenwart, J. Singleton, R. D. Johnson, H. C. Walker, D. T. Adroja, A. D. Hillier, and A. A. Tsirlin, Phys. Rev. B 100, 144432 (2019).
40. J. S. Gardner, M. J. P. Gingras, and J. E. Greedan, Rev. Mod. Phys. 82, 53 (2010).
41. A Bertin and Y Chapuis and P Dalmas de Rotier and A Yaouanc, J. Phys.: Condens. Matter 24, 256003 (2012).
42. S. Gao, O. Zaharko, V. Tsurkan, L. Prodan, E. Riordan, J. Lago, B. Fåk, A. R. Wildes, M. M. Koza, C. Ritter, P. Fouquet, L. Keller, E. Canèvet, M. Medarde, J. Blomgren, C. Johansson, S. R. Giblin, S. Vrtnik, J. Luzar, A. Loidl, C. Ruegg, and T. Fennell, Phys. Rev. Lett. 120, 137201 (2018).
43. D. Reig-i Plessis, A. Cote, S. van Geldern, R. D. Mayrhofer, A. A. Aczel, and G. J. MacDougall, arXiv:1906.10767 (2019).
44. J. Rodriguez-Carvajal, Physica B: Condens. Matter 192, 55 (1993).
45. R. Kajimoto, M. Nakamura, Y. Inamura, F. Mizuno, K. Nakajima, S. Ohira-Kawamura, T. Yokoo, T. Nakatani, R. Maruyama, K. Soyama, K. Shibata, K. Suzuya, S. Sato, K. Aizawa, M. Arai, S. Wakimoto, M. Ishikado, S.-i. Shamoto, M. Fujita, H. Hiraka, K. Ohoyama, K. Yamada, and C.-H. Lee, Journal of the Physical Society of Japan 80, SB025 (2011).
46. M. Ruminy, E. Pomjakushina, K. Iida, K. Kamazawa, D. T. Adroja, U. Stuhr, and T. Fennell, Phys. Rev. B 94, 024430 (2016).
47. M. Nakamura, R. Kajimoto, Y. Inamura, F. Mizuno, M. Fujita, T. Yokoo, and M. Arai, Journal of the Physical Society of Japan 78, 093002 (2009).
48. Y. Inamura, T. Nakatani, J. Suzuki, and T. Otomo, Journal of the Physical Society of Japan 82, SA031 (2013).
49. M. Hutchings (Academic Press, 1964) pp. 227 – 273.
50. S. Rosenkranz, A. P. Ramirez, A. Hayashi, R. J. Cava, R. Siddharthan, and B. S. Shastry, J. Appl. Phys. 87, 5914 (2000).
51. Y. Li, D. Adroja, R. I. Bewley, D. Voneshen, A. A. Tsirlin, P. Gegenwart, and Q. Zhang, Phys. Rev. Lett. 118, 107202 (2017).