Magnetic properties of rare-earth zigzag chain systems $R\text{AgSe}_2$ ($R = \text{Ho}, \text{Er}, \text{Tm}, \text{and} \text{Yb}$)

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Abstract. In an antiferromagnetic zigzag chain, competition between the nearest and next-nearest neighbor interactions could give rise to magnetic frustration. Magnetic semiconductors $R\text{AgSe}_2$ ($R = \text{Ho}, \text{Er}, \text{Tm}, \text{and} \text{Yb}$) crystallize in the ErAgSe$_2$-type orthorhombic structure, where the $R$ ions form a zigzag chain along the orthorhombic $a$-axis. The magnetic susceptibility data for all the samples follow the Curie–Weiss law between 40 and 300 K. The values of the effective magnetic moment $\mu_{\text{eff}}$ are close to those expected for the free $R^{3+}$ ions. Negative values of the paramagnetic Curie temperature $\theta_p$ indicate antiferromagnetic interactions. For $R = \text{Ho}$ and Tm, the specific heat $C(T)$ data exhibit no anomaly down to 0.4 K, which is ascribed to the nonmagnetic singlet ground states under the crystalline electric fields. On the other hand, for $R = \text{Er}$, $C(T)$ shows peaks at $T_1 = 1.3$ K and $T_2 = 0.9$ K, indicating successive antiferromagnetic transitions. For $R = \text{Yb}$, $C(T)$ shows a lambda-type anomaly at $T_m = 1.8$ K. The magnetic entropy at $T_m$ is only 30% of $R \ln 2$ expected for the ground state doublet, suggesting magnetic fluctuations above $T_m$.

1. Introduction
An antiferromagnetic spin-$1/2$ zigzag chain is equivalent to a one-dimensional spin-$1/2$ chain with a nearest neighbor interaction $J_1$ and a next-nearest neighbor interaction $J_2$. In case $J_2$ strongly competes with $J_1$, a long-range antiferromagnetic order could be suppressed to give rise to magnetic frustration. Theoretical simulations with the antiferromagnetic spin-$1/2$ zigzag chain model revealed the manifestation of a variety of nontrivial quantum ground states in magnetic fields such as spin density wave, vector chirality, and $1/3$ magnetization plateau [1, 2].

Recently, a magnetic semiconductor YbCuS$_2$ with an effective spin-$1/2$ Yb zigzag chain was found to exhibit a peculiar antiferromagnetic transition and magnetic-field induced phases [3]. YbCuS$_2$ crystallizes in an orthorhombic structure with the space group of $P2_12_12_1$, where the Yb ions located in deformed sulfur-octahedrons form a zigzag chain along the $a$-axis [4]. The magnetic specific heat $C_m$ exhibits a sharp peak at $T_m = 0.95$ K, where the magnetic entropy is 20% of $R \ln 2$ expected for the Kramers doublet ground state [3]. $T_m$ is robust against the magnetic fields for $B \leq 3$ T, above which the 1/3 magnetization plateau appears, being a characteristic of the up-up-down spin configuration. The $B-T$ phase diagram suggests nontrivial phases arising from the magnetic frustration in the Yb zigzag chain.
Figure 1. (a) Orthorhombic ErAgSe₂-type crystal structure of RAgSe₂ [5]. (b) R zigzag chains along the a-axis with magnetic exchange interactions J₁ and J₂. (c) Powder X-ray diffraction patterns of RAgSe₂ (R = Ho, Er, Tm, and Yb) and a simulated one for R = Yb with the orthorhombic structure. The arrows indicate impurity peaks.

In RAgSe₂ (R = Ho, Er, Tm, and Yb), the R ions are located in slightly deformed sulfur octahedrons [5] and form a zigzag chain along the a-axis as shown in Fig. 1(a) and 1(b). The magnetic susceptibility and the magnetization up to 14 T were previously reported [6]. The magnetic susceptibility data follow the Curie–Weiss law of the trivalent state of the R ions. The paramagnetic Curie temperatures are negative, indicating antiferromagnetic interactions. For T > 4.2 K, no magnetic transition was observed. In the present work, we synthesized polycrystalline samples of these compounds and measured the magnetization M for T ≥ 1.8 K and the specific heat C for T ≥ 0.4 K.

2. Experimental
Polycrystalline samples of RAgSe₂ (R = Ho, Er, Tm, and Yb) were synthesized by melting the constituent elements in evacuated quartz ampoules. The samples were characterized by means of the powder X-ray diffraction analysis and electron-probe microanalysis. Fig. 1(c) shows the X-ray diffraction patterns and a simulation for R = Yb with the ErAgSe₂-type orthorhombic structure [4]. Most peaks can be indexed by the orthorhombic structure [4], while impurity peaks were observed for R = Tm and Yb as indicated by the arrows.

The magnetization was measured between 1.8 K and 300 K in magnetic fields of B ≤ 5 T by using a commercial SQUID magnetometer (Quantum Design, MPMS). The specific heat was measured by the thermal relaxation method using a commercial calorimeter (Quantum Design, PPMS) for 0.4 ≤ T ≤ 300 K and B ≤ 14 T.

3. Results
Figure 2(a) shows the temperature dependence of the magnetic susceptibility M/B of RAgSe₂ for R = Ho, Er, Tm (left-hand scale), and Yb (right-hand scale). The M/B data for R = Ho and Er at T = 1.8 K are much larger than those for R = Tm and Yb. As shown with the open arrow for R = Yb in the inset, a maximum appears at around 3 K. Fig. 2(b) shows the inverse magnetic susceptibility B/M. All the data follow the Curie–Weiss law for 40 ≤ T ≤ 300 K. As shown in Table 1, the values of the effective magnetic moment \( \mu_{\text{eff}} \) are close to those calculated
Figure 2. Temperature dependences of (a) the magnetic susceptibility $M(T)/B$ of $\text{RAgSe}_2$ for $\text{R} = \text{Ho}, \text{Er}, \text{Tm}$ (left-hand scale) and Yb (right-hand scale) in a magnetic field of $B = 0.1$ T. The inset shows the $M(T)/B$ data plotted against a logarithmic scale of the temperature. (b) The inverse magnetic susceptibility $B/M$. The solid lines are the Curie–Weiss fits.

Table 1. Effective magnetic moment $\mu_{\text{eff}}$, the calculated value of $\mu_{\text{cal}}$ for a free $\text{R}^{3+}$ ion, and paramagnetic Curie temperature $\theta_p$ of $\text{RAgSe}_2$ for $\text{R} = \text{Ho}, \text{Er}, \text{Tm},$ and Yb.

| $\text{R}$ | $\mu_{\text{eff}}$ ($\mu_B/\text{f.u.}$) | $\mu_{\text{cal}}$ ($\mu_B/\text{R}^{3+}$) | $\theta_p$ (K) |
|---|---|---|---|
| Ho | 10.59 | 10.58 | -3.6 |
| Er | 9.54 | 9.59 | -2.8 |
| Tm | 7.53 | 7.55 | -15.0 |
| Yb | 4.77 | 4.54 | -71.9 |

for the free $\text{R}^{3+}$ ions. The values of the paramagnetic Curie temperature $\theta_p$ are negative, which indicate antiferromagnetic interactions between the magnetic moments of the $\text{R}^{3+}$ ions. It is noted that the absolute value of $\theta_p$ for $\text{R} = \text{Yb}$ is one order of magnitude larger than those for $\text{R} = \text{Ho}$ and Er. As for the possible reason, the Kondo effect is excluded because of the semiconducting nature.

Figure 3(a) shows the specific heat of $\text{RAgSe}_2$ ($\text{R} = \text{Ho, Er, Tm},$ and Yb). For $\text{R} = \text{Ho}$ and Tm, the $C(T)$ data exhibit no anomaly down to 0.4 K. Figure 3(b) shows the magnetic specific heat $C_m(T)$ which was evaluated by subtracting the $C(T)$ data for $\text{R} = \text{Lu}$ as a phonon contribution from the total $C(T)$ data. $C_m(T)$ for $\text{R} = \text{Ho}$ and Tm are fitted by using a singlet-singlet two-level model. Thereby, we adopted the energy separation of 3.3 and 25 K, respectively, from the crystalline electric field (CEF) nonmagnetic singlet to the excited singlet.

On the other hand, for $\text{R} = \text{Er}$, two peaks appear at $T_1 = 1.3$ K and $T_2 = 0.9$ K. The inset shows the $B$–$T$ phase diagram obtained from the $C(T)$ measurements. As shown in the inset of Fig. 3(a), the two peaks shift to lower temperatures with increasing $B$, indicating successive antiferromagnetic transitions. For $\text{R} = \text{Yb}$, a lambda-type peak appears at $T_m = 1.8$ K. The magnetic entropy at $T_m$ is only 30% of $\text{Rhn2}$ expected for the Kramers doublet ground states, indicating magnetic fluctuations for $T > T_m$. Therefore, the reduction of the magnetic entropy is probably ascribed to magnetic frustration in the Yb zigzag chain as was observed in YbCuS$_2$ [3].

4. Conclusion
We have prepared polycrystalline samples of magnetic semiconductors $\text{RAgSe}_2$ ($\text{R} = \text{Ho, Er, Tm},$ and Yb) and measured the magnetic susceptibility for $T \geq 1.8$ K and the specific heat for
Figure 3. (a) Temperature dependence of the specific heat \(C(T)\) of \(\text{RAgSe}_2\) for \(\text{R} = \text{Ho, Er, Tm, and Yb}\). The inset shows the \(B-T\) phase diagram for \(\text{R} = \text{Er}\). (b) The magnetic specific heat \(C_m(T)\) for \(\text{R} = \text{Ho and Tm}\). The solid lines are calculations with a singlet-singlet two-level model with energy gaps of 3.5 and 25 K for \(\text{R} = \text{Ho and Tm}\), respectively.

\[ T \geq 0.4 \text{ K} \]. The Curie–Weiss fits to the magnetic susceptibility yielded values of the effective magnetic moment \(\mu_{\text{eff}}\) which are close to those expected for the free \(\text{R}^{3+}\) ions. The negative values of \(\theta_p\) indicate antiferromagnetic interactions between the magnetic moments of the \(\text{R}^{3+}\) ions. For \(\text{R} = \text{Ho and Tm}\), no phase transition was observed down to 0.4 K because of the nonmagnetic crystalline electric field (CEF) singlet ground state. On the other hand, magnetic transitions were observed at \(T_1 = 1.3 \text{ K}\) and \(T_2 = 0.9 \text{ K}\) for \(\text{R} = \text{Er}\) and \(T_m = 1.8 \text{ K}\) for \(\text{R} = \text{Yb}\).

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References
[1] Okunishi K and Tonegawa T 2003 J. Phys. Soc. Jpn. 72 479
[2] Hikihara T, Momoi T, Furusaki A and Kawamura H 2010 Phys. Rev. B 81 224433
[3] Ohmagari Y, Onimaru T, Yamane Y, Shimura Y, Umeo K, Takabatake T, Sato H, Kikugawa N, Terashima T, Hirose T and Uji S 2020 J. Phys. Soc. Jpn. 89 093701
[4] Gulay L D, Hucha M, Olekseyuk I, Stepień-Damm J and Pietraszko A 2007 J. Alloys Compd. 428 139
[5] Julien-Pouzol M and Laruelle P 1977 Acta Cryst. B33 1510
[6] Duczmal M and Pokrzywinski S 2001 J. Alloys Compd. 323-324 513