Low Temperature Magnetic Properties of a New Quasi-one-dimensional Organic Magnet α-2-Cl-4-F-V

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Abstract
We examine low-temperature magnetic properties of a new verdazyl radical crystal α-2-Cl-4-F-V. Molecular orbital calculations predict that this material is a spin-1/2 quasi-one-dimensional antiferromagnet; the exchange interaction is strongest in the chains along the b axis, whereas there are three interchain coupling parameters, the ratio of which are 0.06∼0.14 to the intrachain. The magnetization curve at 0.1 K shows gapless behavior like conventional one-dimensional quantum spin systems and saturates at about 5 T. A peak is observed in the temperature dependence of the heat capacity at 0 T, indicating that a three-dimensional ordering occurs at about 0.2 K. On the other hand, the temperature dependence of the magnetization at various magnetic fields shows an anomaly similar to that observed in many of gapped spin systems. This behavior is attributed to the highly frustrated nature of the interchain interactions.

Keywords: quasi-one-dimension; quantum spin; geometrical frustration; verdazyl radical

1 Introduction
Quasi-one-dimensional (Q1D) quantum spin systems have attracted much attention because of a variety of ground states brought by its low dimensionality and strong quantum fluctuation. In particular, the universal properties arising from one dimensionality are described by the Tomonaga-Luttinger liquid (TLL), which is characterized by gapless elementary excitations called spinons and a power-law decay of correlation functions indicating a quasi-long-range order [1]. Spin ladders are one of the best examples for experimental realization of theoretical predictions. For instance, recent studies on the metal-organic compounds (Cu₅H₁₂N)₂CuBr₄ (BPCB) [2, 3] and (Cu₇H₁₀N)₂CuBr₂ (DIMPY) [4, 5] have advanced understanding of a field-induced quantum phase transition from the gapped-spin disordered state to the TTL state.

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These compounds are also of much interest in the context in which the strong-rung and strong-leg coupling regime in the two-leg antiferromagnetic spin ladders can be mapped onto the repulsive and attractive TLL, respectively [3, 5]. Experimental realization of more various Q1D quantum spin systems is thus strongly demanded.

Recently, several verdazyl radical crystals have been synthesized and found to consist of unconventional Q1D magnetic lattices: \(\beta\)-2,6-Cl\(_2\)-V for an Heisenberg antiferromagnetic chain with fourfold periodicity [6], and 3-I-V [7, 8], 3-Br-4-F-V [7, 9], and 3-Cl-4-F-V [7, 10] for \(S = \frac{1}{2}\) ferromagnetic chain based spin-ladders. They are molecular-based crystals, and each of molecules possesses the verdazyl radical carrying an \(S = \frac{1}{2}\) quantum spin. Chemical modification of the verdazyl radical molecule easily enables tuning of the intermolecular interactions, and it is thus useful for realizing Q1D quantum spin systems with unique magnetic properties.

In this paper, we present low-temperature magnetic properties of a new verdazyl radical crystal \(\alpha\)-2-Cl-4-F-V \([3-(2\text{-chloro-4-fluorophenyl})\text{-}1,5\text{-diphenylverdazyl}]\). \textit{Ab initio} molecular orbital (MO) calculations based on the crystallographic data at 25 K predict that the spin lattice model of \(\alpha\)-2-Cl-4-F-V is two-leg ladder structure with geometrical frustration between the ladders. We performed dc magnetization and heat capacity measurements at temperatures between 0.1 K and 2 K in several magnetic fields up to 7 T. Magnetization curve at the base temperature and the temperature dependence of the heat capacity indicate the ground state to be gapless and magnetic. On the other hand, similar to many spin-gapped systems, a broad dip appears in the temperature dependence of the magnetization in several magnetic fields. The strong geometrical frustration predicted by the MO calculations is possibly a cause of the unusual behavior.

2 Experimental

\(\alpha\)-2-Cl-4-F-V was synthesized by a conventional procedure [11], and randomly oriented single crystals with typical dimensions of 4.0 \(\times\) 0.2 \(\times\) 0.2 mm\(^3\) were used in the experiment. The crystal structure was determined by the intensity data collected using a Rigaku AFC-8R mercury charge-coupled device RA-micro7 diffractometer at 25 K. \textit{Ab initio} MO calculations, which provide a powerful approach for investigating the electronic properties of real molecules, were performed using the UB3LYP method as broken-symmetry hybrid density functional theory calculations. All the calculations were performed using the Gaussian 09 program package and 6-31G basis sets. To estimate intermolecular magnetic interactions, we applied the evaluation scheme for multi-spin systems that has been studied previously [12].

The magnetization measurements at temperatures between 0.1 and 2 K were performed using a force magnetometer [13] in static magnetic fields up to 7 T with a \(^3\)He\(^{-}\)\(^4\)He dilution refrigerator. Also, a SQUID magnetometer was used for magnetic susceptibility data above 1.8 K. The specific heat was measured by a quasi-adiabatic method at temperatures down to 0.06 K in several magnetic fields with a dilution refrigerator. In both measurements, a magnetic field is applied perpendicular to the \(b\) axis (see Sec. 3.1).

3 Results and Discussion

3.1 Crystal Structure and Spin Lattice Model for \(\alpha\)-2-Cl-4-F-V

Table 1 shows a summary of the crystallographic data for \(\alpha\)-2-Cl-4-F-V. The MO calculation for single molecule of \(\alpha\)-2-Cl-4-F-V as illustrated in Fig. 1(a) indicates that the spin density
Table 1: Crystallographic data for $\alpha$-2-Cl-4-F-V

<table>
<thead>
<tr>
<th>Formula</th>
<th>$C_{20}H_{15}ClFN_4$</th>
<th>$D_{\text{calc}}/\text{g cm}^{-3}$</th>
<th>1.449</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Temperature</td>
<td>25 K</td>
</tr>
<tr>
<td>Space group</td>
<td>$C2/c$</td>
<td>Radiation</td>
<td>Mo Kα ($\lambda=0.71070$ Å)</td>
</tr>
<tr>
<td>$a$/Å</td>
<td>24.104(5)</td>
<td>Total reflections</td>
<td>2794</td>
</tr>
<tr>
<td>$b$/Å</td>
<td>5.5569(10)</td>
<td>Reflection used</td>
<td>2254</td>
</tr>
<tr>
<td>$c$/Å</td>
<td>25.138(5)</td>
<td>Parameters refined</td>
<td>235</td>
</tr>
<tr>
<td>$\beta$/degrees</td>
<td>95.200(4)</td>
<td>$R \ [I &gt; 2\sigma(I)]$</td>
<td>0.0497</td>
</tr>
<tr>
<td>$V$/Å$^3$</td>
<td>3353.2(11)</td>
<td>$R_w \ [I &gt; 2\sigma(I)]$</td>
<td>0.1121</td>
</tr>
<tr>
<td>$Z$</td>
<td>8</td>
<td>Goodness of fit</td>
<td>1.152</td>
</tr>
</tbody>
</table>

Figure 1: (a) Molecular structure of $\alpha$-2-Cl-4-F-V. (b) Crystal structure of $\alpha$-2-Cl-4-F-V viewed along $c$ axis. Thick solid lines indicate N-C and C-C short contacts associated with the uniform-chain interactions $J_{\text{leg}}$ along $b$ axis. Dotted lines are C-C short contacts associated with the zigzag-chain interactions $J_{\text{zigzag}}$. (c) Other C-C short contacts between the uniform chain. Dash-dotted and dashed lines correspond to the interactions $J_{\text{rung}}$ and $J_{\text{diag}}$, respectively, as shown in Fig. 1(d). (d) Assumed spin lattice model for $\alpha$-2-Cl-4-F-V derived from the MO calculations.

is distributed as follows: about 66% of the total on the verdazyl ring $R_1$, about 15% on each of the $R_2$ and $R_3$ ring, and the rest of about 3% on the $R_4$ ring. This implies that dominant intermolecular interactions are mainly derived from the structural features of the $R_1 \sim R_3$ rings.
As shown in Fig. 1(b), the crystal structure has N-C and C-C short contacts from 3.57 to 3.67 Å between molecules stacking themselves parallel by \( b \) translation, which form a uniform chain structure, and C-C short contacts of 3.68 Å between the \( R_3 \) rings are related by a two-fold screw axis parallel to the \( b \) axis, which connect the uniform chains in a zigzag manner. Figure 1(c) presents that C-C short contacts of 3.49 Å between the \( R_2 \) rings are related by a two-fold rotation axis parallel to the \( b \) axis, which form two-leg ladders together with the uniform chains, and C-C short contacts of 3.70 Å between the \( R_2 \) and \( R_3 \) rings form diagonal interactions in the ladders. From the MO calculations using the crystallographic data at 25 K, dominant intermolecular interactions form the spin lattice as illustrated by Fig. 1(d), to which above short contacts also correspond, and these interactions are evaluated as \( J_{\text{leg}} = 4.70 \text{K} \), \( J_{\text{zigzag}} = -0.68 \text{K} \), \( J_{\text{rung}} = 0.29 \text{K} \), and \( J_{\text{diag}} = 0.24 \text{K} \).

The spin lattice model bears similarity to the “trellis lattice” [14, 15]— a two-leg ladder structure with geometrical frustration — a typical example of which is \( \text{SrCu}_2\text{O}_3 \) [16]. Another important ingredient of the model structure is the \( J_1-J_2 \) coupling with ferromagnetic \( J_1 \) (\( = J_{\text{zigzag}} \)) and antiferromagnetic \( J_2 \) (\( = J_{\text{leg}} \)) [17, 18]. The \( J_1-J_2 \) model has recently attracted much attention since unusual magnetic phase transitions in a magnetic field have been found in the model compounds such as \( \text{LiCuVO}_4 \) [19]. Validity of the model structure is discussed later with the magnetic properties of \( \alpha \)-2-Cl-4-F-V.

### 3.2 Magnetic Susceptibility

Figure 2(a) shows the magnetic susceptibility \( \chi = M/H \) at temperatures between 1.8 and 300 K in 0.1 T. The diamagnetic contribution of \( \alpha \)-2-Cl-4-F-V, calculated to be \(-1.357 \times 10^{-4} \text{emu/mol} \) by Pascal’s constants, is subtracted. From the linear fit of \( 1/\chi \) at above 15 K to the Curie-Weiss law as shown in the inset of Fig. 2(a), a Weiss temperature \( \Theta \) and an effective Bohr magneton number \( p_{\text{eff}} \) is estimated to be \(-2.36 \text{K} \) and \( 1.66 \), respectively. In typical verdazyl radical crystals, the \( g \)-factor is isotropic so that \( g \sim 2 \) and \( p_{\text{eff}} \sim 1.73 \). The

![Figure 2](image-url)
a New Quasi-one-dimensional Organic Magnet $\alpha$-2-Cl-4-F-V

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reduction in $p_{\text{eff}}$ is attributed to non-magnetic impurities.

At about 2 K, $\chi$ exhibits a broad maximum as typically seen in quasi-one-dimensional compounds. Considering the intrachain interaction is predominant at above 1.8 K, we fit the Bonner-Fisher curve [20] to the susceptibility data as indicated in Fig. 2(a). It yields the intrachain interaction of 3.1 K, close to the calculated value $J_{\text{leg}} = 4.70$ K.

### 3.3 Field Dependence of the Magnetization at the Base Temperature

The field dependence of the magnetization at 0.1 K is shown in Fig. 2(b). The magnetization is increasing monotonously with increasing field to the saturation, analogous to archetypal magnetization curve of a one-dimensional Heisenberg antiferromagnet (HAF) (e.g., Ref. [21]). Judging from the field derivative of the magnetization, the saturation field $H_s$ is about 4.7 T. Applying the expression of the saturation field in a spin-1/2 one-dimensional HAF, $H_s = 2J/g\mu_B$ [20, 22], with the estimated intrachain interaction from the Bonner-Fisher curve fitting ($J = 3.1$ K), $H_s$ is estimated to be 4.61 T, which is consistent with the magnetization data. This indicates that the intrachain interactions are indeed predominant in $\alpha$-2-Cl-4-F-V.

Note that there is a small upturn in the $dM/dH$ data at below 0.5 T. This might be due to a phase transition or a paramagnetic impurity contribution. The impurity contribution, if any, is only about 1% of the saturation magnetization.

### 3.4 Temperature Dependence of the Specific Heat and Magnetization in Magnetic Fields

Significant features differing from those of the spin-1/2 one-dimensional HAF appear in the temperature dependence of the specific heat ($C_{\text{mag}}/T$) and magnetization ($M(T)/H$) (Fig. 3). As we can see in Fig. 3(a), the temperature variation of $C_{\text{mag}}/T$ at zero field exhibits a peak at about 0.1 K, which can be ascribed to a three-dimensional magnetic ordering. The temperature at which the peak occurs ($T_N$) increases with increasing field, and the peak height becomes most pronounced at 0.5 T. Note that the nuclear Schottky contributions from $^1$H and $^{19}$F in finite fields are subtracted (see the inset of Fig. 3(a)).

However, the temperature dependence of $M/H$ in the same field range has no appreciable anomaly except for the minimum at slightly above $T_N$ (Fig. 3(b)). The position of the minimum slightly shifts with increasing field as indicated, and vanishes at 2 T. Paramagnetic impurities, the magnetic moment of which is at most 1% of the saturation magnetization as mentioned before, cannot account for this low-temperature upturn in $M(T)/H$.

### 3.5 Further Discussion

An analogous dip in the temperature dependence of the magnetization can be seen in some quasi-one-dimensional systems. In the case of spin-gapped systems, a crossover into the low-temperature TLL regime has been shown by numerical calculations for spin-1 Haldane chains [23] and spin-1/2 two-leg ladders [24, 25]. Experimentally, such behavior has been observed in DIMPY [4] and Ni(C$_5$H$_{14}$N$_2$)$_2$N$_3$(PF$_6$) (NDMAP) [26]. It thus seems plausible that the two-leg ladder structure exists in the spin lattice model of $\alpha$-2-Cl-4-F-V. However, for the two-leg spin-1/2 antiferromagnetic ladder, it is predicted that the ground state becomes a gapped disordered state so long as interchain interactions are nonzero [27]. On the other hand, the existence of a three-dimensional magnetic phase transition in a zero field indicate that the ground state of $\alpha$-2-Cl-4-F-V to be magnetic. The strong geometrical frustration predicted by the MO calculations might account for the suppression of the gap. Note that numerical
Figure 3: (a) Temperature dependence of the magnetic specific heat \((C_{\text{mag}}/T)\). Arrows indicate temperatures at which the \(C_{\text{mag}}/T\) takes the peak \((T_N)\). Inset: raw data of the specific heat \((C/T)\) (open circles) and estimated nuclear specific heat \((C_{\text{nuc}}/T)\) (dotted line) at 1.5 T. (b) Temperature dependence of the magnetization \((M(T)/H)\). For clarity, there are some offsets on the graph in several magnetic fields as shown in the legend. Arrows indicate the temperatures at which the \(M(T)/H\) takes the minimum value.

calculations for the “trellis lattice” model with all interactions being antiferromagnetic predict that magnetically-ordered ground states can occur when \(J_{\text{zigzag}}\) and \(J_{\text{rung}}\) are comparable to each other [28]. Whether such a minimum appears in \(M(T)\) when a spin gap is suppressed due to frustration remains to be clarified.

The spin structure in the three-dimensional ordering state is another issue. In two-leg ladder compounds, the long-range ordering state can often be described by the magnon Bose-Einstein condensation [29]. In this situation, strong geometrical frustration can induce an incommensurate ordering state. If the \(J_1-J_2\) model as discussed in Sec. 3.1 is applicable, a helical ordering state would occur [18]. Microscopic measurements such as nuclear magnetic resonance would thus be needed for further elucidation of the ordering state of \(\alpha\)-2-Cl-4-F-V.

4 Summary

A new quasi-one-dimensional organic magnet \(\alpha\)-2-Cl-4-F-V has been synthesized, and dc magnetization and specific-heat measurements at low temperatures are performed. \textit{Ab initio} MO calculations predict that the compound has a spin-lattice structure analogous to the “trellis lattice” model. The magnetization curve at 0.1 K shows gapless behavior, and the temperature dependence of the specific heat indicates that a magnetic ordering exists in zero magnetic field. On the other hand, the temperature dependence of the magnetization at low fields shows an anomaly similar to the gapped spin systems, having a non-magnetic disordered ground state. These unusual behavior could be attributed to strong geometrical frustration in the spin lattice. Further investigations using microscopic measurements are needed to identify the magnetic ground state.
Acknowledgements

Y. K. and T. S were supported by KAKENHI grants from Japan Society for the Promotion of Science (Grant Numbers: 24340075, 15H03682).

References


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