

**BaCu<sub>2</sub>V<sub>2</sub>O<sub>8</sub>: Quasi-one-dimensional alternating chain compound with a large spin gap**

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The new quasi-one-dimensional spin gap compound BaCu<sub>2</sub>V<sub>2</sub>O<sub>8</sub> was studied by means of magnetic susceptibility and heat capacity measurements on a powder sample. The magnetic susceptibility was well reproduced by alternating antiferromagnetic chain model with  $J_1=260$  K and  $J_2=52$  K, which result in a large spin gap of about 230 K. It is suggested that the  $J_1$  and  $J_2$  are ascribable to interactions along the Cu-O-V-O-Cu path and the Cu-O-Cu path, respectively.

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The search for one-dimensional (1D) quantum spin systems has been a very active field of condensed matter physics, due to discoveries of various fascinating magnetic phenomena related to spin and charge correlations. These systems mainly include the spin-Peierls (SP) transition, the two-leg spin ladder, the spin alternating chain and charge ordering,<sup>1</sup> which are characterized by ground states of the spin singlet with a finite spin gap due to their spin quantum effect. Among all 1D spin systems, the linear spin chain compounds have attracted much theoretic and experimental interest. Their exotic magnetic properties have been intensively studied. For the uniform linear spin chain compound CuGeO<sub>3</sub>,<sup>2</sup> it was found that the opening of a spin gap is due to a structural phase transition from a gapless state into a gapped state, which accompanies a spontaneous lattice dimerization below its critical temperature. For the alternating spin chain compound (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, it was found that two different spin gaps coexist, and that the second spin gap is about twice as large as the first one.<sup>3</sup>

In order to understand the exotic magnetic phenomena of 1D linear chain systems, theoretic and experimental studies have been carried out by means of various methods. For CuGeO<sub>3</sub>, current interest is the observation of antiferromagnetic (AF) order induced by various substitutions.<sup>4,5</sup> Among these doping effects, Si<sup>4+</sup> doping implies that GeO<sub>4</sub> tetrahedra plays an important role in SP transition of CuGeO<sub>3</sub>, because a small amount of Si<sup>4+</sup> doping on Ge<sup>4+</sup> site can suppress SP state, without any changes of Cu<sup>2+</sup> site and crystal structure.<sup>6,7</sup> For (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, the structural analysis<sup>8</sup> and NMR measurement<sup>9</sup> indicated that the coexistence of two different energy gaps are due to the appearance of two different linear chains related to positional arrangement of the PO<sub>4</sub> tetrahedra, in contrast to the high-pressure phase which has only a single spin gap of about 27 K.<sup>10</sup> These findings indicate a fact that the magnetic properties of 1D spin gap systems may be strongly affected by a nonmagnetic tetrahedral sublattice.

Recently, the depression of SP phase and the appearance of AF phase below the SP transition temperature were observed in various impurity-doped CuGeO<sub>3</sub>.<sup>11</sup> Further, the existence of a first-order phase transition between dimerized-AF and uniform-AF phases was also observed with the increasing of impurity doping concentration.<sup>12</sup> In addition, it is found that the depression of spin gap  $\Delta$ , which

accompanies the appearance of various AF phases, is linear relation with the increasing of impurity doping.<sup>13</sup> Therefore, it is suggested that a large spin gap  $\Delta$  is favorable for the increasing of impurity doping concentration, which maybe attract much scientific interest for investigation of new magnetic phenomena. Unfortunately, for linear spin chain systems, no compounds are found to have a large spin gap over 200 K.

These reasons led us to develop a new linear spin chain compound with a large spin gap by considering the appropriate nonmagnetic tetrahedral sublattices. The inorganic compounds of copper oxides with Cu<sup>2+</sup> ( $d^9$ ) are found that their structural features are well defined toward quasi-one-dimensional spin systems, in which the Cu<sup>2+</sup> ions are bridged by oxygen ions. It is also found that the V<sup>5+</sup> ( $d^0$ ) ions are similar to Ge<sup>4+</sup> and P<sup>5+</sup> ions, which can be tetrahedrally coordinated by oxygen ions. Quite recently, in our search for new spin gap compounds based on copper and vanadium complex oxides, we found that BaCu<sub>2</sub>V<sub>2</sub>O<sub>8</sub> has two important magnetic interaction paths, which, from the viewpoint of structure, are like those of (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. Our experimental results of magnetic susceptibility and heat capacity measurement indicated that the spin degrees of freedom of this compound are in a nonmagnetic ground state with a spin gap of about 230 K. To our knowledge, this is the first time that a spin gap over 200 K for spin-1/2 Heisenberg AF alternating chain systems has been observed. Further, it is also one of good examples for understanding of the role of nonmagnetic tetrahedral sublattices in linear spin chain systems.

The crystal structure of BaCu<sub>2</sub>V<sub>2</sub>O<sub>8</sub> is similar to SrNi<sub>2</sub>V<sub>2</sub>O<sub>8</sub> and has tetragonal symmetry of space group *I*-42*d* with  $a=12.774$  Å,  $c=8.148$  Å, and  $Z=8$ .<sup>14</sup> Due to a strong Jahn-Teller effect, the Cu<sup>2+</sup> ( $d^9, S=1/2$ ) ions have quasipolar (4+1+1)-coordination bridged by oxygen ions, while the V<sup>5+</sup> ions ( $d^0, S=0$ ) have two crystallographic sites V<sub>1</sub> and V<sub>2</sub>, which are tetrahedrally coordinated by oxygen ions. As shown in Fig. 1, the most prominent feature is that the one-dimensional linear chains are made of edge-sharing pairs of CuO<sub>4</sub> square-plaquettes and the VO<sub>4</sub> tetrahedra (V<sub>1</sub> site) along the *c* axis, and the linear chains are separated by another VO<sub>4</sub> tetrahedra (V<sub>2</sub> site). The present results suggest that two major AF interactions are important similar to those in (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>; one through the almost orthogonal Cu-O-Cu paths ( $J_2$ ), the other mediated by the almost linear

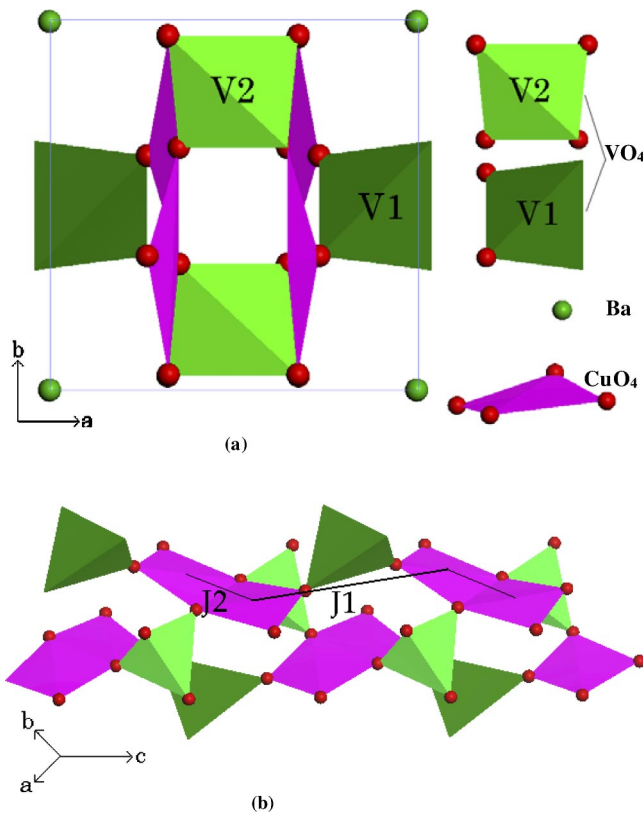


FIG. 1. (Color online) The crystal structure of BaCu<sub>2</sub>V<sub>2</sub>O<sub>8</sub> ( $0.5a \times 0.5b \times 2.5c$ ). (a) The V<sup>5+</sup> ions have two crystallographic sites V<sub>1</sub> and V<sub>2</sub>, corresponding to the VO<sub>4</sub> tetrahedra, (dark) and (light). (b) Two interaction paths, ( $J_1$ ) and ( $J_2$ ), of the linear chain built by VO<sub>4</sub> tetrahedra (V<sub>1</sub>) and edge-sharing pairs of CuO<sub>4</sub> square-plaquettes along the  $c$ -axis.

Cu-O-V-O-Cu ( $J_1$ ), and that interactions of interchains resulting from their 90° Cu-O-V-O-Cu paths are negligible.

A polycrystalline sample was synthesized by a conventional solid-state reaction method using high purity reagents of BaCO<sub>3</sub> (4N), CuO (4N), and V<sub>2</sub>O<sub>5</sub> (4N) as starting materials. The reagents were mixed in stoichiometric proportion with ethanol and calcined at 993 K in an O<sub>2</sub> flow for 60 h with several intermediate grindings. Finally, the powder samples were pressed into pellets and sintered at 1023 K in an O<sub>2</sub> flow for 24 h, and then cooled to room temperature at a rate of 100 K/h. No impurity phase was observed by powder x-ray diffraction (XRD) measurement using Cu  $K\alpha$  radiation. The crystalline parameters refined by the Rietveld method using the RIETAN-2000 program<sup>15</sup> are in good agreement with those reported previously.<sup>14</sup> The dc magnetic susceptibility was measured with a superconducting quantum interference device (MPMS5S, Quantum Design) magnetometer in a magnetic field of 1 T from 2 K to 400 K and a magnetic balance (MB-2, Shimadzu) from 400 K to 900 K on heating. The magnetization was measured with the applied field up to 9 T at 2 K using a commercial physical property measurement system (PPMS, Quantum Design). The heat capacity was measured by a relaxation method using PPMS.

The large open circles in Fig. 2 show the temperature dependence of magnetic susceptibility of the sample

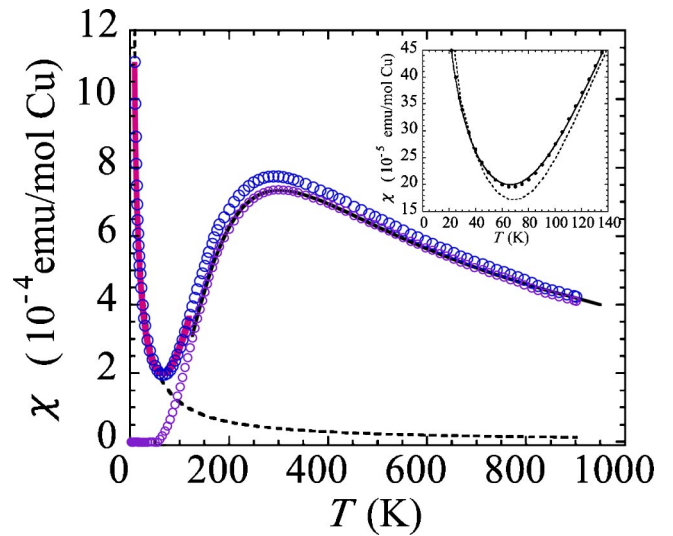


FIG. 2. (Color online) Temperature dependence of magnetic susceptibility of BaCu<sub>2</sub>V<sub>2</sub>O<sub>8</sub> from 900 K to 2 K. The big open circles represent the observed raw data, the small open circles are the data after subtraction of the Curie-term. The thick solid line represents the result of fitting to the equation,  $\chi(T) = \chi_0 + \chi_{\text{cw}}(T) + \chi_{\text{spin}}(T)$  below 120 K. The thin solid line represents the result of fitting to the chain model given by Hatfield above 120 K. The dashed line represents the Curie-term. The inset shows a comparison of fitted results between the isolated dimer model and the chain model. The closed circles represent the observed data, the solid line the fitted result by the chain model, and the dashed line the fitted result by the isolated dimer model.

BaCu<sub>2</sub>V<sub>2</sub>O<sub>8</sub>. A broad maximum was observed around 280 K, which displays the 1 D nature in magnetism. The susceptibility decreases rapidly with decreasing temperature, while a sudden upturn appears below 60 K. The data below 120 K were fitted well to  $\chi(T) = \chi_0 + \chi_{\text{cw}}(T) + \chi_{\text{spin}}(T)$  as shown in Fig. 2, where  $\chi_0$  is the temperature-independent term,  $\chi_{\text{cw}}(T) = C/(T - \theta)$  the Curie-Weiss term corresponding to the upturn below 60 K, and  $\chi_{\text{spin}}(T) = aT^{-1/2} \exp(-\Delta/T)$  the susceptibility of one-dimensional chain systems with a finite spin gap  $\Delta$ .<sup>16</sup> The parameters were obtained as follows:  $\chi_0 = -8.31 \times 10^{-5}$  emu/mol Cu,  $\theta = -0.25$  K,  $C = 1.08 \times 10^{-2}$  emu K/mol Cu,  $a = 3.39 \times 10^{-2}$ , and  $\Delta \approx 230$  K. The obtained  $\chi_0$  value is close to the sum of core diamagnetic susceptibilities,  $-7.50 \times 10^{-5}$  emu/mol Cu. Taking account of the small magnitude of  $\theta$  and no detection of impurity by XRD, it is natural to consider that the upturn below 60 K originates from the isolated Cu<sup>2+</sup> ions possibly due to lattice defect. In fact, magnetization vs applied field curve measured at 2 K is well reproduced by Brillouin function of  $S = 1/2$  as shown in Fig. 3. The fraction of the isolated Cu<sup>2+</sup> ions estimated from the saturation magnetization, 2.8%, is very close to that, 2.9%, estimated from Curie constant  $C$ .

Plotted with small open circles in Fig. 2 is what is approximately regarded as the component of the susceptibility due to the Cu<sup>2+</sup> spin system ( $\chi_{\text{spin}}$ ), as estimated by subtracting the Curie-Weiss term and the temperature-independent term. The continuous decrease of  $\chi_{\text{spin}}$  toward zero with a decrease in temperature reveals the existence of an energy gap in the spin excitation spectrum. Further, the  $\chi_{\text{spin}}$  above

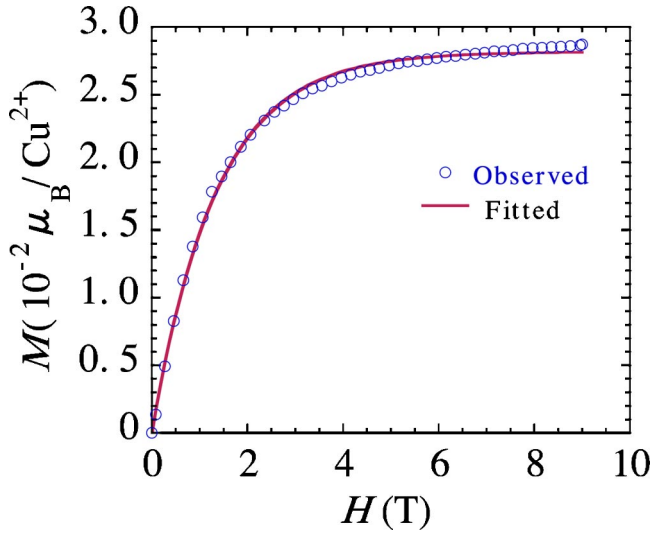


FIG. 3. (Color online) Magnetization ( $M$ ) vs applied field ( $H$ ) at 2 K. The open circles represent the observed raw data, the solid line the fitted value by a Brillouin-function of  $S=1/2$ .

120 K could be well fitted to an analytical equation of the alternating chain model proposed by Hatfield,<sup>17,18</sup>

$$\chi_{\text{spin}}(T) = \frac{Ng^2\mu_B^2}{k_B T} \frac{0.25 - 0.08\chi + 0.004\chi^2}{1 + 0.39\chi - 0.006\chi^2 + 0.49\chi^3}, \quad (1)$$

where  $\chi = |J|/k_B T$ . We obtained  $J_1/k_B T = 260$  K,  $\alpha = 0.2$ , and  $g = 2.22$  for a valid temperature range  $T \geq 0.465J_1$ . For the alternating chain systems, the spin gap for magnetic spin excitations from the  $S=0$  singlet ground state to the lowest  $S=1$  triplet excited states can be approximately expressed as follows:<sup>19</sup>

$$\Delta = J_1(1 - \alpha)^{3/4}(1 + \alpha)^{1/4}, \quad (2)$$

where  $\alpha = J_2/J_1$  ( $0 \leq \alpha \leq 0.9$ ). According to this analytical equation, the spin gap  $\Delta$  is estimated to be about 230 K. This result is in good agreement with that estimated from low temperature data mentioned above.

Considering that the alternation parameter  $\alpha$  is 0.2, this material is quite close to an isolated dimer ( $\alpha=0$ ). Then, we also fit the observed raw data to the dimer model as expressed as follows:<sup>16</sup>

$$\chi(T) = \chi_0 + C/(T - \theta) + \chi_{\text{dimer}}(T), \quad (3)$$

where

$$\chi_{\text{dimer}}(T) = Ng^2\mu_B^2/k_B T [3 + \exp(\Delta/T)]. \quad (4)$$

The solid and dashed lines in the inset of Fig. 2 show the results of fitting to the dimer model and the chain model, respectively. It is clear that the reproducibility by the dimer model is poorer than that of the chain model at low temperature. This finding suggests that the chain model is most suitable for BaCu<sub>2</sub>V<sub>2</sub>O<sub>8</sub>.

Figure 4 shows the temperature dependence of heat capacity. There was no  $\lambda$ -like anomaly in the heat capacity

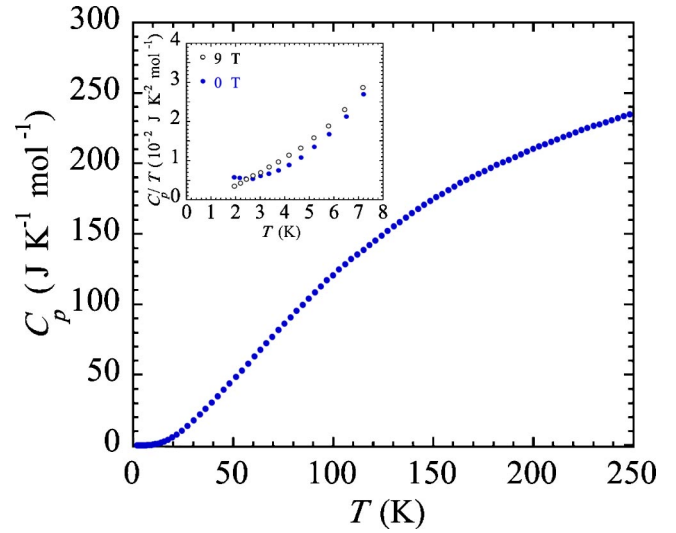


FIG. 4. (Color online) Heat capacity of BaCu<sub>2</sub>V<sub>2</sub>O<sub>8</sub> as a function of temperature. The inset shows  $C_p/T$  vs  $T$ , a comparison of heat capacities measured under the fields 0 and 9 T below 8 K.

from 250 K down to 2 K. This finding supports the absence of a phase transition and the nature of a nonmagnetic ground state. For alternating chain systems with a spin gap, the magnetic specific heat at low temperature ( $T \ll \Delta$ ) can be expressed as  $C_m(T) \propto J_1(\Delta/T)^{3/2}[1 + (T/\Delta) + 0.75(T/\Delta)^2]e^{-\Delta/T}$ .<sup>16</sup> It is shown that the magnetic contribution  $C_m$  is dominated by the spin gap  $\Delta$  and the interaction exchange  $J_1$ . We found that the value of  $C_m$  of BaCu<sub>2</sub>V<sub>2</sub>O<sub>8</sub> below 8 K is very small ( $< 10^{-8}$  J/mol K), by using  $J_1 = 260$  K and  $\Delta = 230$  K, and that the observed heat capacity  $C_p$  almost results from the lattice contribution corresponding to  $\beta_1 T^3$  at low temperature. As observed in (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>,<sup>10</sup> the inset of Fig. 4 also shows that the small upturn below 3 K observed under 0 T, which would be attributed to the free Cu<sup>2+</sup> spins, was suppressed by the increasing of an applied field 9 T.

The data on magnetic susceptibility and heat capacity shows that the spin degrees of freedom of BaCu<sub>2</sub>V<sub>2</sub>O<sub>8</sub> are in a nonmagnetic ground state with a spin gap of about 230 K. It is also suggested that the 1D alternating chain model is suitable for this compound. For 1D alternating chain systems with a spin gap, according to the approximate analytical equation (2) mentioned above, it was shown that the existence and magnitude of the spin gap are determined by the larger interaction exchange  $J_1$  and the alternation parameter  $\alpha$  related to the difference of the two interactions  $J_1$  and  $J_2$ . Usually, for many transition metal compounds, the magnitude and sign of the spin interaction exchange are determined by the microscopic spatial coordination of magnetic ions and oxygen ligands containing so-called corner-sharing and edge-sharing configurations, according to Goodenough's rules.<sup>20</sup> Although the bridging angle of the Cu-O-Cu path in BaCu<sub>2</sub>V<sub>2</sub>O<sub>8</sub> is  $\sim 94^\circ$  of almost orthogonal, it is reasonable to suppose that the superexchange interaction of the Cu-O-Cu path is AF, because theoretical study on CuGeO<sub>3</sub> suggested that the nonmagnetic tetrahedral sublattice can strongly affect this interaction and change the sign of superexchange interaction of the  $90^\circ$  Cu-O-Cu path from ferromagnetic to

AF.<sup>21</sup> The AF interaction of the  $\sim 94^\circ$  Cu-O-Cu bond was recently reported in  $\text{Cu}_2\text{UO}_2(\text{PO}_4)_2$ .<sup>22</sup> Further, as shown in Fig. 1, it is also suggested that the edge-sharing pairs of  $\text{CuO}_4$  square-plaquettes in alternating linear chain are non-coplanar, which presumably affects this interaction. On the other hand, it is well known that the superexchange interactions of the  $90^\circ$  Cu-O-Cu bond are very weak, in fact, the spin gaps of  $\text{CuNb}_2\text{O}_6$  (Ref. 23) and  $\text{SrCu}_2(\text{BO}_3)_2$ ,<sup>24</sup> which are dominated by superexchange interactions of almost  $90^\circ$  Cu-O-Cu, are smaller than 50 K. However, NMR measurement on the copper vanadate  $\text{LiCuVO}_4$  suggested that in contrast to Cu-O-Cu paths, the interaction along the Cu-O-V-O-Cu paths is strong, because mixing of the vanadium  $4s$  orbital with oxygen  $2s$  and  $2p$  results in a transfer of magnetic  $d$ -spin from the  $\text{Cu}^{2+}$   $e_g$  orbital onto the  $\text{V}^{5+}$   $4s$  orbital.<sup>25</sup> Further, it is also proposed that the super-superexchange interactions involving the linear Cu-O—O-Cu paths are strong, due to the favorable spatial position.<sup>26</sup> Based on above discussions, it is reasonable to suggest that the  $\text{VO}_4$  tetrahedral sublattice maybe affects the interaction of almost  $90^\circ$  Cu-O-Cu, and that the  $J_2$  results from almost

orthogonal Cu-O-Cu paths, whereas the  $J_1$  results from almost linear Cu-O-V-O-Cu paths. This finding is also similar to  $(\text{VO})_2\text{P}_2\text{O}_7$ , which has a major AF interaction of the V-O-P-O-V paths between a pair of  $\text{VO}_5$  pyramids mediated by  $\text{PO}_4$  tetrahedra and a minor interaction of the V-O-V paths between a pair of edge-sharing  $\text{VO}_5$  pyramids.<sup>3</sup>

In conclusion, it was found that  $\text{BaCu}_2\text{V}_2\text{O}_8$  displays the 1D nature in magnetism and has a nonmagnetic ground state with a spin gap of about 230 K. The experimental magnetic susceptibility was well reproduced by alternating chain model with the  $J_1=260$  K and  $J_2=52$  K. Based on a comparison with the similar magnetic interaction path of  $(\text{VO})_2\text{P}_2\text{O}_7$ , it is suggested that the  $J_1$  and  $J_2$  are ascribable to interactions along the Cu-O-V-O-Cu path and the Cu-O-Cu path, respectively, and that large  $J_1$  and small  $J_2/J_1$  result in a large spin gap. The results also suggested that the nonmagnetic  $\text{VO}_4$  tetrahedral sublattices play an important role in the alternating linear chain of the titled material.

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