Proceedings of Japan-France Seminar
J. Phys. Soc. Jpn. **65** (1996) Suppl. B pp. 146-150

Magnetic Properties of $CeNiAl_4$; a Non-Magnetic Heavy Fermion

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The crystal structure of $CeNiAl_4$ is an orthorhombic $YNiAl_4$ type. The electrical resistivity, magnetization, thermoelectric power, magnetic susceptibility of a single crystal $CeNiAl_4$ were measured. $CeNiAl_4$ is a non-magnetic dense-Kondo compound with an electronic specific heat coefficient $\gamma = 175$ mJ/mol·K^2 and Kondo temperature $T_K = 99$ K. The electrical and magnetic properties show the large anisotropic behavior reflecting the crystal structure. We have calculated the magnetic susceptibilities to get information of the crystal-electric-field splitting.

KEYWORDS: $CeNiAl_4$, Heavy-fermion, valence-fluctuation

§1. Introduction

For a few decades the issues of the highly correlated 4f electron systems have been intensively investigated and huge experimental results have been accumulated. $CeCu_6$[1)] is one of the most typical examples belonging to heavy electron regime with a non-magnetic ground state and the electronic specific-heat coefficient reaches about 1600mJ/mol·K^2 at the lowest temperature. The 4f electrons have been described, roughly speaking as the coherent Kondo lattice, in which the 4f electrons have been dealt as localized electron. In contrast, CeNi[2)] is one of the typical examples belonging to the valence fluctuation regime with a non-magnetic ground state and the γ–value is 85mJ/mol·K^2 at low temperature. Two examples are situated on both extreme of 4f electron state with a non-magnetic ground state; 4f electron is atomic on one side and itinerant on another side. Recently much attentions are focused on compounds having an *intermediate* γ-value between 100 and a few hundred mJ/mol·K^2. Superconductor $CeCu_2Si_2$[3)] has the γ-value of about 100mJ/mol·K^2 above the superconducting transition temperature. CeNiSn[4)] is semimetallic and the γ-value is about 200mJ/mol·K^2 above the gap-opening temperature. $CeNiAl_4$, on which experiments have been started by Mizushima *et al.*, is non-magnetic and the γ-value is 175mJ/mol·K^2. $CeNiAl_4$ became an example of an *intermediate* heavy fermion compound with a non-magnetic ground state. In this paper, we analyzed our data of magnetic susceptibility by the crystal-electric-field(CEF) theory taking into account the Kondo effect. On the basis of the obtained CEF levels of Ce 4f electron, we review our experimental results hitherto published on $CeNiAl_4$ together with new data of thermoelectric power.

§2. Experimental Procedure

The prepared sample of $CeNiAl_4$ was confirmed to have the orthorhombic $YNiAl_4$ type structure[5)] by powder X-ray diffraction. Details of sample preparations and the method of measurements of electrical resistivity, magnetization and specific heat are described in our previous publications.[6)] Thermoelectric power was measured by a pair of Au-Fe/chromel thermo-couple attached to both ends of the sample length in the temperature range between 1.8 and 300K.

§3. Experimental Results

3.1 Electrical resistivity.

Figure 1 shows the ln*T* dependence of the electrical resistivity on the a, b and c axes. In our last report,[6)] measurement was carried out in the temperature range from 2K to 300K. In this report, the temperature was extended down to 0.1K with the use of a dilution refrigerator for the a and b axes. No anomaly due to magnetic transition was seen at least down to 0.1K, the lowest temperature of our measurement. The electrical resistivity of all axes increases with decreasing temperature from room temperature and reaches a

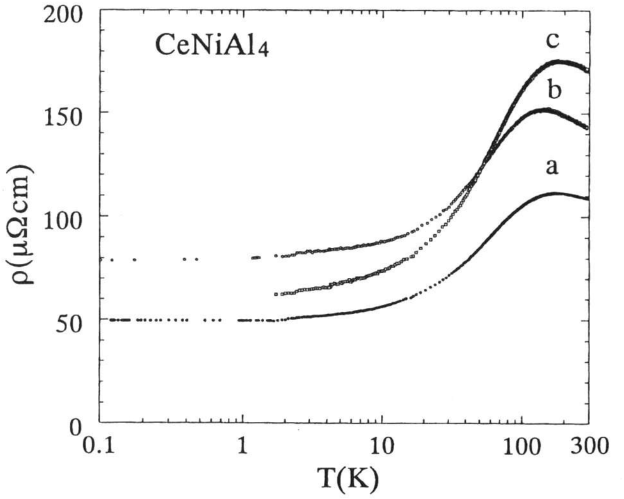

Fig.1. The ln*T* dependence of the electrical resistivity of the single-crystal $CeNiAl_4$ on the a, b and c axes.

maximum at around 150K. With further decreasing temperature, the electrical resistivity steeply decreases.

3.2 Magnetic susceptibility and magnetizations

Figure 2 shows the temperature dependence of the reciprocal susceptibilities of a, b and c axes. The temperature dependence of all three axes above 100K obeys the Curie-Weiss law with an effective magnetic moment $\mu_{eff}=2.53\mu_B$, which is close to the free Ce^{3+} ion value. The extrapolation of the Curie-Weiss fitting gives the three different paramagnetic Curie temperatures; θ_a= -57K, θ_b=-174K and θ_c=-364K. An average value of three paramagnetic Curie temperatures is -198K. We can say with fair certainty that this large negative paramagnetic Curie temperature is due to Kondo effect, because the magnetic transition was not observed in the measurement of the electrical resistivity and magnetic susceptibility. The Kondo temperature T_K was roughly estimated to be 99K using the relation $T_K=|\theta_P|/2$ for a single-impurity problem.[7]

Figure 3 shows the magnetization process on the a, b and c axes up to 7.6T at 1.8K. The magnetizations at maximum field on all axes are smaller than the theoretical value which was calculated from crystal-electric-field calculation. Magnetization reduction cannot be understood by crystal-electric-field effect only. It may be explained by a strong mixing effect and/or by the Kondo effect.

3.3 Specific heat

Figure 4 shows the T^2 dependence of the specific heat divided by temperature C/T. An anomaly at 2.4K is likely to come from T_N of antiferromagnetic $CeAl_2$, because a few small lines due to $CeAl_2$ were found in the diffraction pattern by an X-ray diffractometer having a high resolution. These lines due to $CeAl_2$ were not detected in our last report,[6] where a diffractometer having a standard resolution has been used. Besides the ratio of the entropy for anomaly to $R\ln 2$ is only 3%. Thus we neglected it. The γ value was estimated as $175 mJ/mol\cdot K^2$, by the linear

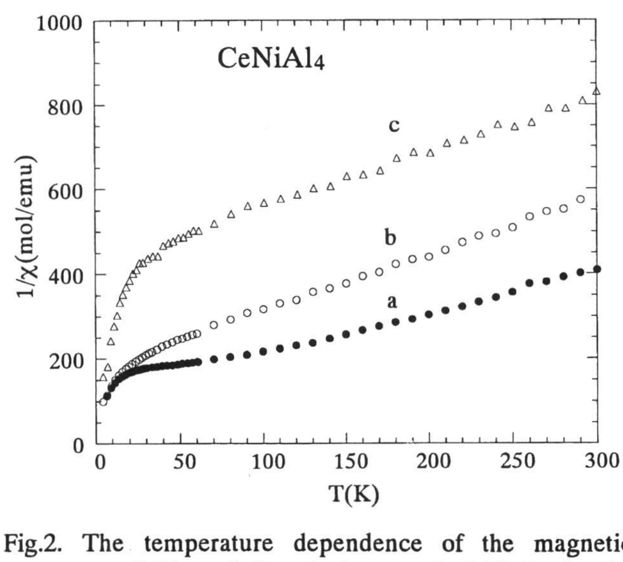

Fig.2. The temperature dependence of the magnetic susceptibility of the single-crystal $CeNiAl_4$ in the magnetic fields parallel to a, b and c axes.

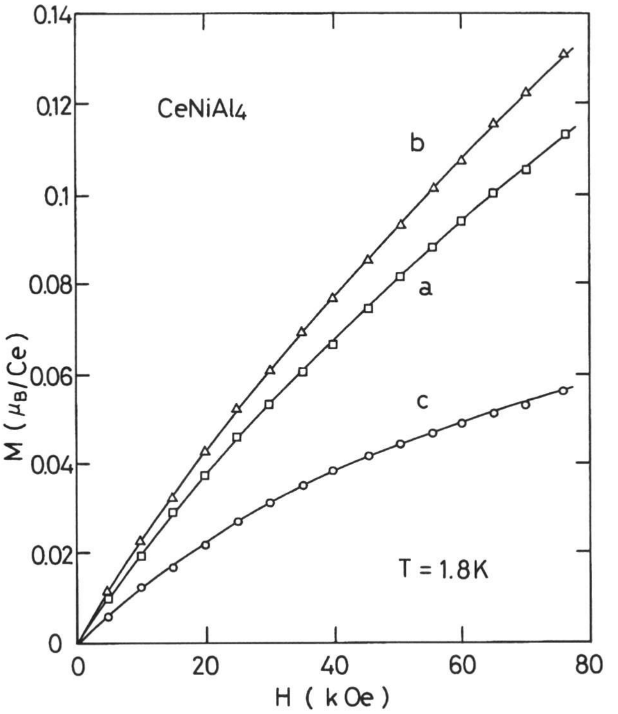

Fig.3. Magnetization process of the single-crystal $CeNiAl_4$ at 1.8K in the fields parallel to a, b and c axes.

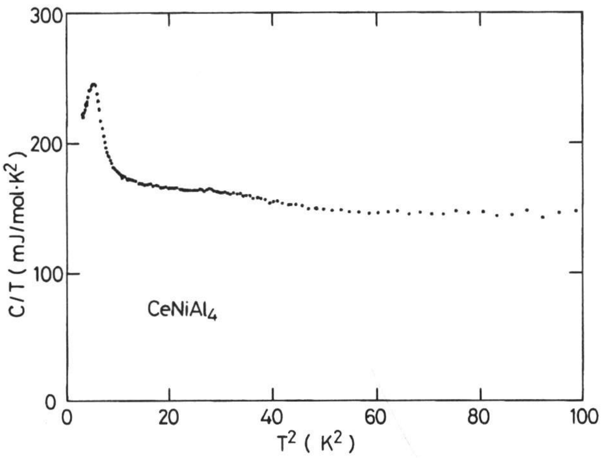

Fig.4. Specific heat divided by T vs. T^2 of $CeNiAl_4$.

extrapolation to the absolute zero temperature. This γ value is not as large as one of $CeCu_6$ ($1600 mJ/mol\cdot K^2$)[8] which is well known as heavy fermion compound. However, it is not as small as those of $CeSn_3$ ($53 mJ/mol\cdot K^2$)[9] or CeNi ($85 mJ/mol\cdot K^2$) which are known as valence fluctuation compounds with high T_K. It seems reasonable to suppose that $CeNiAl_4$ belongs to the category of intermediate between heavy fermion and valence fluctuation regime.

Figure 5 shows the temperature dependence of the entropy S. The entropy at 20K reaches only $3.5 J/mol\cdot K$ which is 60% of $R\ln 2$. Thus, one can say that Kramers' doublet has partly disappeared in this temperature range.

3.4 Thermoelectric power

Figure 6 shows the temperature dependence of

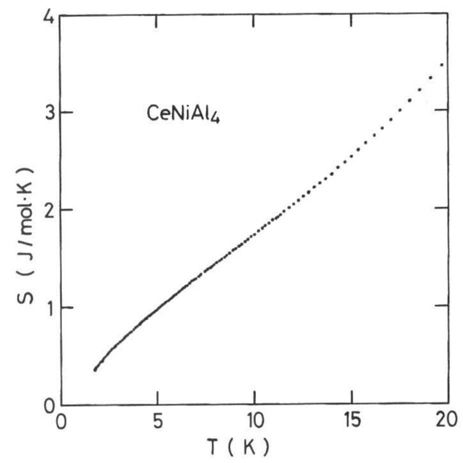

Fig.5. The temperature dependence of entropy of single-crystal CeNiAl4.

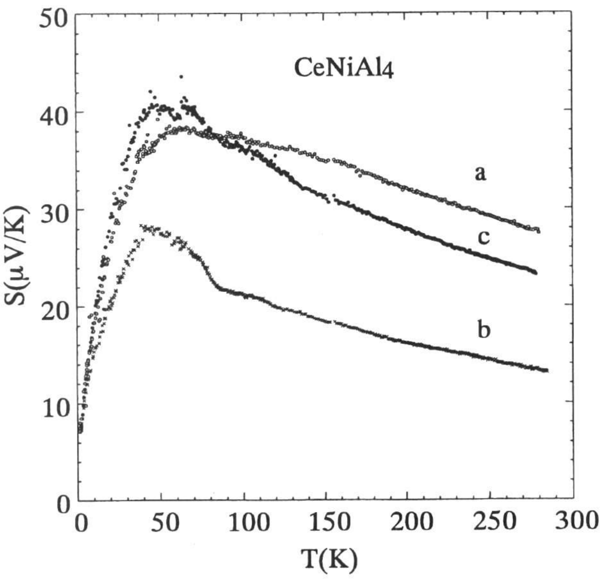

Fig.6. The temperature dependence of the thermoelectric power of single-crystal CeNiAl4 on a, b and c axes.

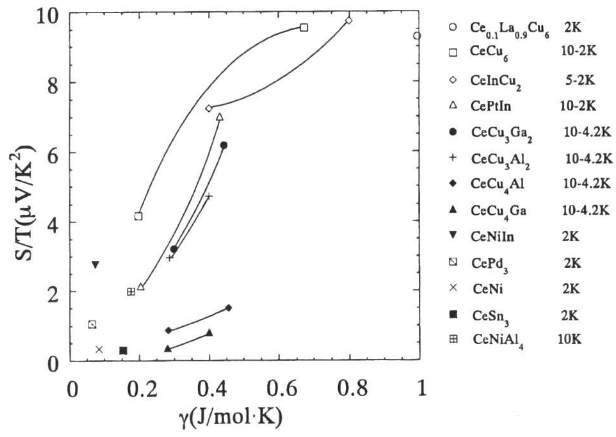

Fig.7 The thermoelectric power divided by the temperature S/T as a function of the electronic specific heat coefficient γ for some of the heavy fermion compounds and the intermediate valence compounds from ref.(13). The values of the temperatures listed in the right margin denote the temperatures at which the values of S/T were calculated. The value of CeNiAl4 is added in the present study.

thermoelectric powers of a, b and c axes. They show the broad peaks at around 50K, with their maximum values of 30~40μV/K. Overall behaviors are similar to those of CeNi[10], CePd3[11] and CeSn3[12]. The thermoelectric power divided by temperature S/T for several Ce compounds correlates closely with the electronic specific heat coefficient γ.[13] In the case of CeNiAl4, the value of S/T at 10K was obtained to be about 2. We added the value of CeNiAl4 in the figure 7, S/T vs. γ, worked by Sakurai.[13] Thus, it becomes evident that CeNiAl4 take a position between the valence fluctuation compounds and the heavy fermion compounds.

§4. Analysis and Discussion

4.1 Crystal-electric-field effect

The level scheme of crystal electric field was estimated by analyzing the temperature dependence of reciprocal susceptibility. Operator method was used for analyzing. In general, the hamiltonian under a magnetic field H is expressed as

$$H = H_{CEF} + H_{Zeeman}$$

where H_{CEF} is CEF hamiltonian, and H_{Zeeman} is Zeeman term. Here, CEF hamiltonian is expressed as

$$H_{CEF} = \sum_{n,m} B_n^m C_n^m \qquad (1)$$

In the case of Ce^{3+}, function (1) has expansion

$$H_{CEF} = B_2^0 C_2^0 + B_2^2 C_2^2 + B_2^{-2} C_2^{-2} + B_4^0 C_4^0 + B_4^2 C_4^2 + B_4^{-2} C_4^{-2} + B_4^4 C_4^4 + B_4^{-4} C_4^{-4}$$

where B_n^m are CEF coefficients and C_n^m are irreducible spherical tensors.[14] The reciprocal susceptibility is expressed as

$$\frac{1}{\chi} = \frac{1}{\chi_{CEF}} + \lambda \qquad (2)$$

χ_{CEF}^{-1} is the reciprocal susceptibility and λ is a parameter of the molecular field and/or the Kondo effect. We fitted the reciprocal susceptibility of (2) to experimental values marked by black circles in figure 8. Figure 8 shows the results marked by thin lines that were calculated with the parameters of set 1 and set 2 in Table I. All second and forth order parameters were used in the case of set 1, but the uncertainty of B_4^4 is large. Therefore we took B_4^4=0 and the best values of parameters were obtained in set 2. As shown in the Table I, we can say that the parameters of set 2 are better than those of set 1, because each error of parameter of set 2 is smaller than those of set 1. In both cases of set 1 and set 2, the energy level Δ_1 and Δ_2, splittings from ground state to the first exited state and to the second excited state of the CEF, were estimated to be

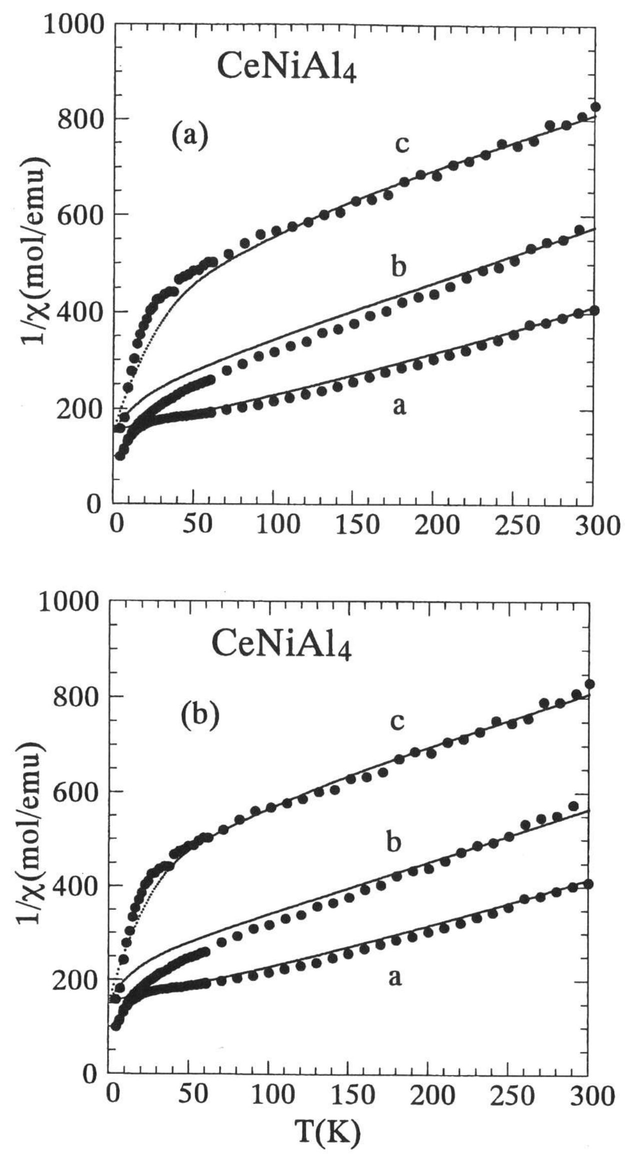

Fig.8. The temperature dependence of the reciprocal susceptibility of the single-crystal $CeNiAl_4$ in the magnetic fields parallel to a, b and c axes. Thin lines are the calculated ones using the parameters of set 1 in (a) and set 2 in (b). See text.

almost same values. The values of Δ_1 and Δ_2 are 166K and 584K in set 2. The eigenfunctions and J_Z corresponding to each state of set 1 and set 2 is indicated in table I. The molecular field λ parameter was obtained to be 155 mol/emu. Those of the other Kondo compounds are reported as, for example, 55mol/emu for $CeCu_2Si_2$[15], 70mol/emu for $CeCu_2$.[16] In general, one can understand that large value is a feature of Kondo compounds. The one of $CeNiAl_4$ was, however, found to be particularly enormous.

4.2 T_K, γ and Δ

The -ln$T$ behavior of electrical resistivity above 150K should be due to Kondo effect. Here, we consider two theories, one by Cornut *et al.*[17] and the other by Maekawa *et al.*.[18] Cornut *et al.* have calculated the

Table I. B_n^m are the CEF coefficient. $\Delta 1$ and $\Delta 2$ are the first and second excited state in CEF. λ is the molecular field parameter. Numbers in blanket are uncertainties.

	B_2^0	B_2^2	B_4^0	B_4^2	B_4^4	λ	$\Delta 1$	$\Delta 2$
			(K)			(mol/emu)	(K)	
set 1	-949 (76)	407 (23)	310 (287)	-683 (740)	137 (1080)	155	168	615
set 2	-933 (30)	361 (13)	286 (88)	-606 (88)	0	155	166	584

Table Ⅱ. Crystal field energy levels, eigenfunctions and magnetizations at each levels from fitting to the reciprocal susceptibility.

Energy(K)	Eigenfunction	$J_z(\mu_B)$
584	$0.95\left\|\pm\frac{5}{2}\right\rangle-0.31\left\|\pm\frac{1}{2}\right\rangle+0.03\left\|\mp\frac{3}{2}\right\rangle$	2.3
166	$0.97\left\|\pm\frac{3}{2}\right\rangle-0.23\left\|\mp\frac{1}{2}\right\rangle-0.11\left\|\mp\frac{5}{2}\right\rangle$	1.3
0	$0.92\left\|\pm\frac{1}{2}\right\rangle+0.29\left\|\pm\frac{5}{2}\right\rangle+0.25\left\|\mp\frac{3}{2}\right\rangle$	0.54

temperature dependence of spin-disorder of Ce-based intermetallic compounds using the third-order perturbation theory. Electrical resistivity seems to have a maximum at a temperature corresponding to, but smaller than the CEF splitting. On the other hand, according to Maekawa *et al.*, the temperature dependence of electrical resistivity has a broad peak at temperature which is much lower than the CEF splitting. In the case of the $CeNiAl_4$, electrical resistivity increases with decreasing the temperature from room temperature and then shows a maximum around 150K. This peak temperature is nearly equal to Δ_1=166K, and is much smaller than Δ_2=584K, the values obtained from the calculation of susceptibility. According to both theories, the peak of electrical resistivity is understood as an indication of the Kondo state under the CEF splitting with the temperature of the maximum reflecting the CEF splitting.

The drastic decrease of ρ for temperature below 150K may be understood as a sign of coherent Kondo lattice.

We have shown that the magnetic susceptibility of $CeNiAl_4$ can be analyzed by the CEF theory of a localized 4f electron. However, the appearance of large magnetic moment at low temperature range was suppressed by a large value of θ_p due to Kondo effect. Also, magnetization at 1.8K under a magnetic field of 7.6T was much smaller than that of expected from the CEF theory as explained already.(see Table Ⅱ)

We got a result that the temperature dependence of thermoelectric power of $CeNiAl_4$ was similar to those of CeNi, $CePd_3$, and $CeSn_3$, the typical valence fluctuation compounds. The temperature of the positive peak of thermoelectric power for these valence fluctuation compound may be understood as the Kondo temperature T_K. Thus, if $CeNiAl_4$ is a valence fluctuation compound, the value of T_K is estimated to be 50K.

On the other hand, Bhattacharjee *et al.*[19] consider thermoelectric power of Kondo compounds under CEF effect and they showed that a peak of thermoelectric power appears at temperature range between roughly $\Delta/6$ and $\Delta/3$. Here, Δ is over-all splitting. The value of Δ was obtained to be 584K for $CeNiAl_4$ in the Table I from calculation of susceptibility. Therefore, we can also consider that the peak temperature corresponds to a temperature of $\Delta/6$.

We noted before that $CeNiAl_4$ belongs to the category of intermediate between heavy fermion and valence fluctuation regime on the basis of the value of γ of the compound. Corresponding to this notion, our all measurements, electrical resistivity, thermoelectric power, magnetic susceptibility and magnetization carried out on $CeNiAl_4$, have indeed shown behaviors which are on the half way between those of the heavy fermion compounds and the valence fluctuation compounds.

We can probably expect metamagnetic transition for $CeNiAl_4$ as well as $CeCu_6$ and $CeRu_2Si_2$. On the basis of the equation $g\mu_B H = k_B T_K$[20], taking T_K as 99K from the value of θ_P, we estimated the critical field of metamagnetic transition to be 74T.

In summary, $CeNiAl_4$ is an example of intermediate heavy fermion compound with a non-magnetic ground state. Furthermore, it is speculated that metamagnetic transition occurs at around 74T.

The authors would like to thank Dr. T.Kuwai who measured electrical resistivity below 2K using a dilution refrigerator of the Grenoble type.

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