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The linear birefringence and magnetic specific heat of the two-dimensional Ising disordered antiferromagnet $K_2Cu_xCo_{1-x}F_4$

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Abstract. We report on the temperature dependence of the optical linear birefringence (LB) of the mixed 2d Ising magnet $K_2Cu_xCo_{1-x}F_4$. The temperature dependence of the Co–Co pair contribution to the specific heat, proportional to that of the corresponding temperature derivative of the LB, is deduced for samples over the whole range of concentration $0 < x < 1$. The long-range λ-type anomaly has been shown to vanish for $x_c > 0.2$, i.e. far below the percolation limit $x_p = 0.5$, a result which was predicted from calculations for 2d disordered Ising magnets, but never checked experimentally.

1. Introduction

In recent years many theoretical and experimental works have been devoted to the study of the thermodynamics and phase transitions of disordered magnetic systems. It is now well established that sharp phase transitions are still present in magnetic and non-magnetic impurity-doped magnets. As compared to the pure case, different critical exponents are predicted for disordered compounds by the Harris criterion [1] if the specific heat critical exponent α is positive. This criterion is inconclusive in the case of randomly dilute two-dimensional (2d) Ising systems, for which $\alpha = 0$.

Only few experimental data have been reported so far on the thermodynamic properties of disordered 2d Ising compounds [2–5] in spite of their interesting marginal behaviour. The random-site [6] and random-bond [7] dilute 2d nearest-neighbour Ising models on honeycomb or square lattices have been treated theoretically. These calculations and simulations [8] reveal drastic changes of the specific heat with dilution but no experimental proof of this particular behaviour has been reported so far.

In this paper, we report on the determination of the linear birefringence (LB), a quantity related to the magnetic energy E_m, and hence of the associated specific heat C_m in the random-exchange dilute 2d Ising quadratic and transparent antiferromagnet $K_2Cu_xCo_{1-x}F_4$, over the whole mixing range ($0 < x < 1$). The LB is defined as $\Delta n = n_c - n_a$, i.e. the difference between the optical indices of refraction relative to the two principal $\boldsymbol{c}$- and $\boldsymbol{a}$-axes of the crystal; the light is then propagating along the other $\boldsymbol{a}$-axis. The magnetic contribution to the LB, often much larger than that of the lattice, is found to be proportional to E_m either in pure [9] or in diamagnetically substituted transparent antiferromagnets [3, 10, 11].

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2. Experimental procedure

In real disordered materials, the critical divergence of the specific heat at the transition temperature is always limited by macroscopic concentration fluctuations. An advantage of the investigation of the magnetic energy via LB in disordered magnets comes from the ability to perform measurements over a limited well defined small area of the sample, which minimizes the contribution of concentration gradients. The effect of sample inhomogeneity along the $\boldsymbol{c}$-axis is reduced by placing a small pinhole in front of the sample. Moreover, as a consequence of the growth process, the concentration is undoubtedly uniform over the sample within $\boldsymbol{c}$-planes, i.e. along the light direction. In measurements, the temperature inhomogeneity over the sample volume investigated is estimated to be less than 0.05 K.

K_2CoF_4 has a body-centred tetragonal structure, whereas for K_2CuF_4 this structure is slightly distorted by a cooperative Jahn–Teller effect, providing an alternate elongation of the F^- octahedra surrounding the Cu^{2+} ions along the two principal axes in the $\boldsymbol{c}$-plane. K_2CoF_4 ($T_N = 107.85$ K) is considered as the archetype of 2d Ising ($S = 1/2$) antiferromagnets with a very weak interlayer exchange interaction ($J'/J = 10^{-6}$) while the 2d ($S = 1/2$) ferromagnetism in K_2CuF_4 ($T_c = 6.25$ K) results from the alternate arrangement of $d_{z^2-x^2}$ and $d_{z^2-y^2}$ ground-state orbitals. $K_2Cu_xCo_{1-x}F_4$ forms a good solid solution for all values of x [12]. Down to $x_{JT} = 0.41$, the cooperative Jahn–Teller distortion of CuF_6 octahedra is present, but for $x < x_{JT}$ a non-cooperative or dynamic Jahn–Teller effect is still operative. Strong 2d magnetic frustration due to competing exchange interactions strongly affects its (x, T) magnetic phase diagram [12] as compared with that of the site-diluted isomorphic compound $K_2Mg_xCo_{1-x}F_4$. Evidence for even a spin-glass phase at low temperature has been obtained for the intermediate $0.5 < x < 0.84$ concentration range, located between the disordered antiferromagnetic ($x < x_p = 0.5$) and complex ferromagnetic ($x > x_F = 0.84$) phases. As revealed by static susceptibility measurements [12], up to x_F a strong anisotropy, parallel to the $\boldsymbol{c}$-axis, still persists in mixed compounds.

Assuming a random-site distribution of Co and Cu spins over the lattice, one can express the Ising Hamiltonian for a site-disordered system by

$$H = -2\sum_{\langle i,j\rangle} J_{ij} S_i^z S_j^z \tag{1}$$

with a bound distribution probability

$$\begin{aligned} P(J_{ij}) = {} & (1-x)^2\delta(J_{ij} - J_{Co-Co}) + x(1-x)\delta(J_{ij} - J_{Cu-Co}^{AF}) \\ & + x(1-x)\delta(J_{ij} - J_{Cu-Co}^{F}) + x^2\delta(J_{ij} - J_{Cu-Cu}) \end{aligned} \tag{2}$$

where J_{A-B} represents the exchange coupling between A and B ions. The superscripts AF and F distinguish the two kinds of antiferromagnetic and ferromagnetic Cu–Co bond, respectively. The exchange interactions for symmetric pairs of ions have been determined in the pure compounds: $J_{Co-Co} = -92$ K and $J_{Cu-Cu} = 11.2$ K. Because of the lack of precise information on the $J_{Cu-Co}^{(AF\text{ or }F)}$ exchange interactions in $K_2Cu_xCo_{1-x}F_4$ we can only assume that $J_{Cu-Co}^{AF} + J_{Cu-Co}^{F} < -55 \pm 25$ K, a rough estimate deduced from the high-field magnetization data [13]. Both Co–Co and Cu–Co interactions are strongly Ising-like in character [12, 14]. In conclusion, $K_2Cu_xCo_{1-x}F_4$ can be considered as a nearly ideal 2d Ising ($S = 1/2$) disordered system on a square lattice with nearest-neighbour competing interactions. As discussed below, it is better described by random-bond theories than by more intuitive random-site models.

The antiferromagnetic order is not much perturbed under large fields; for example, our SQUID magnetometer measurements demonstrate that the temperature dependence of the

static magnetic susceptibility of $K_2Cu_{0.33}Co_{0.67}F_4$ is similar under small (1 Oe) and large (11.8 kOe) [12] applied fields, as previously reported for $Rb_2Mg_{0.3}Co_{0.7}F_4$ [15].

As shown for $K_2Cu_xMn_{1-x}F_4$ [16], the LB is not formally proportional to the magnetic energy in compounds containing two types of magnetic ion. Assuming that the individual magnetic contributions to the LB for each kind of pair (α), $\Delta n_m(\alpha)$, are proportional to individual magnetic energy terms E_m^α [9], one may write for the total LB

$$\Delta n_m = \sum_\alpha \Delta n_m(\alpha) = \sum_\alpha B_\alpha P(\alpha) E_m^\alpha \tag{3}$$

where the $P(\alpha)$s represent the different bonding probabilities (i.e. x^2 for Cu–Cu pairs) appearing in expression (2). The B_α-coefficients depend upon optical transition probabilities and are functions of the photon energy considered. Thus, expression (3) differs from that for the total magnetic energy:

$$E_m = \sum_\alpha P(\alpha) E_m^\alpha. \tag{4}$$

However, since the four main exchange integrals J_α have significantly different absolute values for in $K_2Cu_xCo_{1-x}F_4$, one expects to distinguish the individual contributions E_m^α as a function of temperature. As in the case of $K_2Cu_xMn_{1-x}F_4$ [16] the thermal variation of each individual $\mathrm{d}(\Delta n_m(\alpha))/\mathrm{d}T$ term can be assigned to the corresponding $\mathrm{d}E_m^\alpha/\mathrm{d}T$ contribution in the expression for the total specific heat.

A test of the homogeneity of our samples has been performed by chemical analyses on several parts of each crystal. Thus we have estimated (table 1) their concentration gradient over the optical cross section range studied, i.e. limited by a diaphragm 0.2 mm in diameter. The experimental method used to measure the LB, as a function of temperature, has been described previously in a paper on $K_2Cu_xZn_{1-x}F_4$ [10].

3. Results and discussion

The temperature dependence of the LB in $K_2Cu_xCo_{1-x}F_4$ samples having different concentrations ($0 < x < 1$) is reported in figures 1(a) and 2(a). The curves can be decomposed into two contributions: one coming from the lattice part Δn_l, the thermal variation of which is assumed to follow a Debye law, and the other from the magnetic part Δn_m, related to individual variations of the magnetic energy for the different pairs of magnetic ions (see expression (3)). As often verified [9], the lattice contribution to the LB, due to the thermal variation of the lattice expansion and that of the electron–phonon interaction, is weak as compared to the magnetic part.

Our LB data related to Co–Co pairs of ions are comparable to the results of calculations of the magnetic energy in disordered 2d Ising systems by Monte Carlo simulations [8]. In usual magnetic specific heat measurements it is generally not possible to deduce the Schottky anomaly in such disordered magnetic compounds because of the too-large lattice contribution at high temperature; this is clearly exhibited for $Rb_2Co_{1-x}Mg_xF_4$ [2]. Much more efficient at high temperature, the lattice contribution to the LB changes sign from pure K_2CuF_4 to K_2CoF_4; its magnitude varies monotonically on increasing x in $K_2Cu_xCo_{1-x}F_4$ (figures 1(a) and 2(a)). This behaviour is closely related to the modification of the Jahn–Teller distortion with disorder, as already discussed for $K_2Cu_xZn_{1-x}F_4$ [10] compounds. The magnetic contribution $\Delta n_m(T, x)$ can be calculated from the expression

$$\Delta n_m(T, x) = \Delta n(T, x) - \Delta n_l(T, x) \tag{5}$$

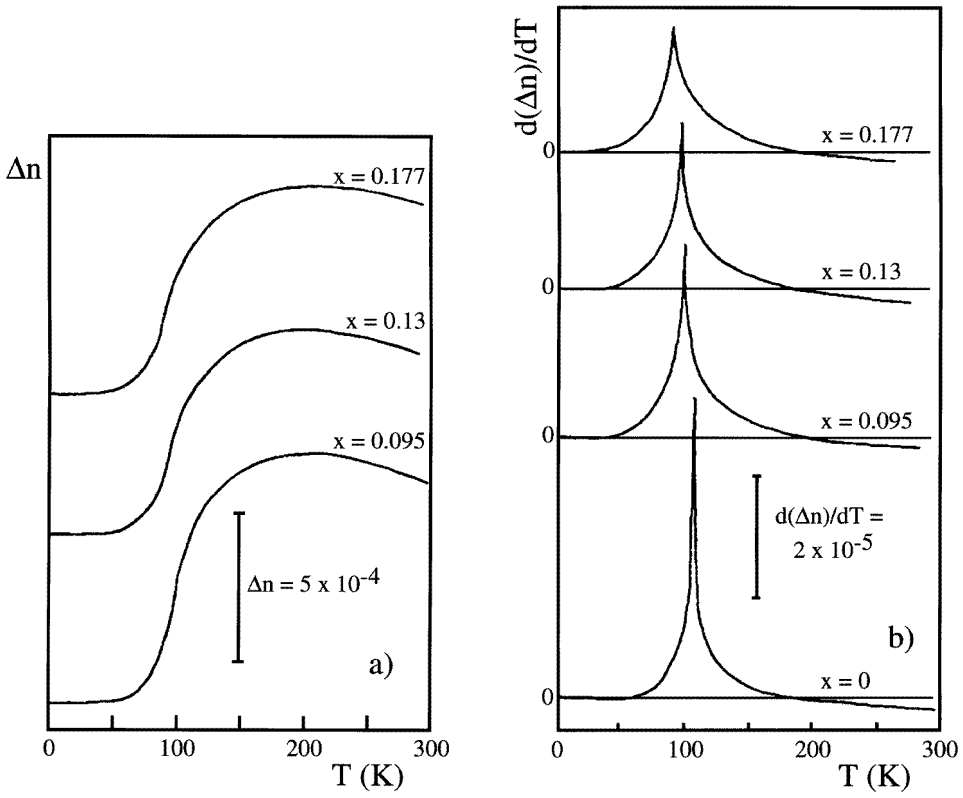

Figure 1. The temperature dependence of the linear birefringence (a) and of the temperature derivative of the birefringence (b) for $K_2Cu_xCo_{1-x}F_4$ samples (small x-values). The $d(\Delta n)/dT$ curve is also shown for the pure K_2CoF_4 compound [18].

where $\Delta n(T, x)$ is the measured birefringence. It is usually assumed that the lattice contribution is proportional to $\Delta n_l(T)$ for the diamagnetic K_2ZnF_4 isomorphic compound [10].

A family of $d(\Delta n)/dT$ curves have been deduced from the LB data for all concentrations studied (figures 1(b) and 2(b)); the reported set of curves is close to the representation of $d(\Delta n_{m)}/dT$ ones, because of the negligible contribution of the lattice. As previously discussed, the $d(\Delta n_{m)}/dT$ temperature dependences for the pure K_2CuF_4 and K_2CoF_4 samples are similar to that of the magnetic specific heat $C_m(T)$ for the 2d Heisenberg ($S = 1/2$) ferromagnet and the 2d Ising ($S = 1/2$) antiferromagnet, respectively [10, 17, 18]. For the mixed compound $K_2Cu_xCo_{1-x}F_4$, from expression (3), one can also write

$$d(\Delta n_m)/dT = \sum_\alpha B_\alpha P(\alpha) C_m^\alpha. \tag{6}$$

For significantly different J_α-values, the individual magnetic specific heat anomalies, related to different pairs of interacting magnetic ions, may be well separated from the $d(\Delta n_m)/dT$ temperature variation. The $d(\Delta n_m)/dT$ (or specific heat) anomaly appearing at high temperature is due to pairs of Co ions; it vanishes gradually as x increases, in agreement with the probability of having Co–Co pairs (expression (2)) at the expense of the low-temperature anomalies related to Cu–Cu and Cu–Co pairs of ions. For $x = 1$,

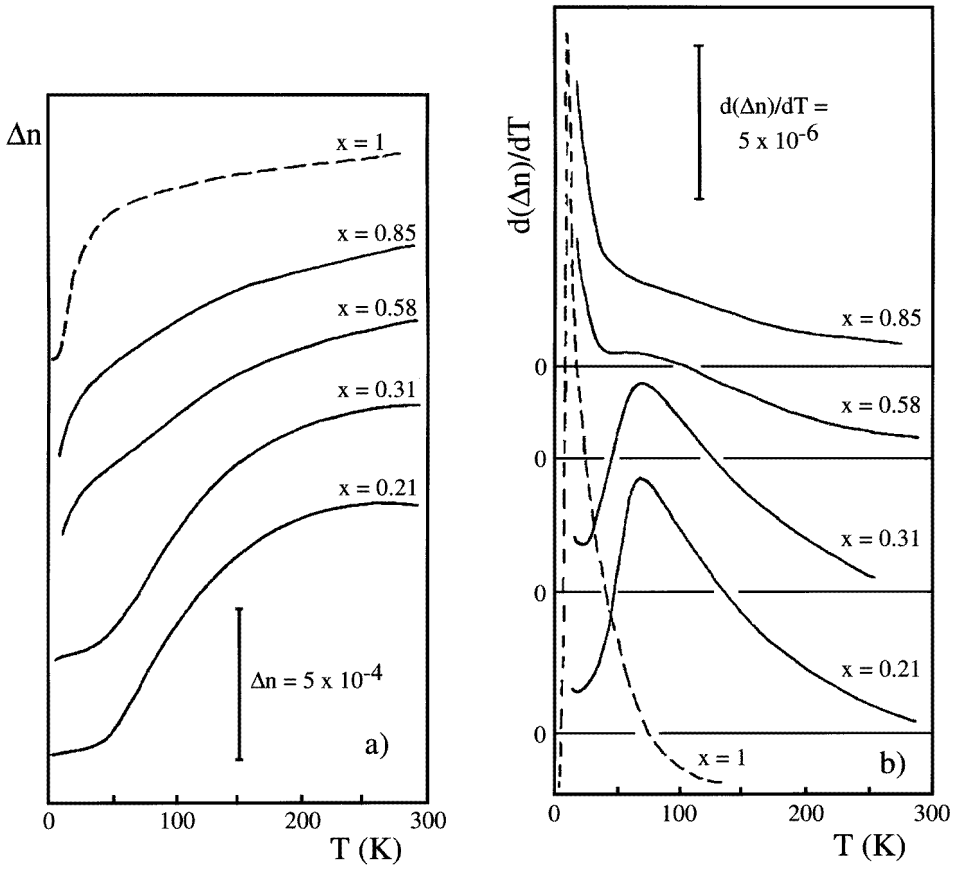

Figure 2. The temperature dependence of the linear birefringence (a) and of the temperature derivative of the linear birefringence (b) of $K_2Cu_xCo_{1-x}F_4$ (intermediate and large x-values). The data are also reported for the pure K_2CuF_4 compound [9].

the specific anomaly due to ferromagnetically coupled Cu–Cu pairs is entirely recovered [10, 16]; its disappearance, in the range of composition $0.31 < x < 0.58$ (figure 2(b)), is consistent with the vanishing of the cooperative Jahn–Teller effect at $x_{JT} = 0.41$ [10, 12]. The $\mathrm{d}(\Delta n_m)/\mathrm{d}T$ Schottky anomalies for Cu–Co pairs are not evident at the expected temperatures; this is probably a result of too-weak coefficients B_{Cu-Co} (expression (3)).

Onsager's exact solution for the 2d Ising model predicts a huge divergence of the specific heat anomaly at T_N in agreement with the temperature dependence of $\mathrm{d}(\Delta n_m)/\mathrm{d}T$ for pure K_2CoF_4 (figure 1(b) and [17, 18]). A drastic decrease of the sharp C_m^{Co-Co} λ-type anomaly at small copper dilution is well revealed when comparing the data for $x = 0.095$ to the pure K_2CoF_4 case. On increasing the Cu impurity content, T_N is depressed, and more and more entropy is transferred into the short-range-order term. The amplitude of the λ-peak is found to decrease drastically with dilution very much faster than x^2, the scaling factor of the Cu–Cu magnetic energy term (expression (2)). Then, this behaviour is much more emphasized for our disordered 2d Ising compound than in $d = 3$ random-exchange Ising magnets [11]. Even the long-range-order anomaly vanishes at $x \sim x_c = 0.2$ (figures 1(b) and 2(b)); as soon as T_N becomes smaller than $|J/k|$ the long-range-order peak disappears

completely at the expense of the broad Co–Co Schottky-type anomaly [19]. Such an effect is also present in 3d Ising disordered compounds [11], but the critical λ-type anomaly is found to vanish only at the percolation threshold.

This experimental smearing of the transition at x_c (figure 2(b)), far below $x_p = 0.5$, is also evident from renormalization group calculations in a randomly bond-dilute 2d nearest-neighbour Ising model on the square lattice [7] or from calculations on the honeycomb lattice [6]. Note that these calculations, developed for dilute ferromagnets, are valid for disordered 2d Ising antiferromagnets in zero field, as well [6]. Monte Carlo simulations [8] on a site-dilute 2d Ising model strongly confirm this behaviour.

As pointed out and discussed by de Jongh [19] a strong similarity of behaviour is expected between a 2d Ising disordered compound and a coupled system of magnetic chains in a 2d infinite magnetic percolation cluster, for which the dependence of the specific heat on interchain coupling has been calculated by Onsager. A dilute 2d system can be represented by a network of 1d macrobonds which cross one another at nodes separated by a mean characteristic length ξ_p. As a consequence, for $x > x_c$, the critical region becomes so narrow that the λ-type sharp anomaly is no longer visible, so the temperature variation of the specific heat $C_m(T)$ is then well described only by a Schottky anomaly. As discussed for the bond-dilute model [7], the dramatic critical-region narrowing near $x = x_c$ is controlled by the crossover exponent φ from pure to random-exchange Ising models:

$$|t_M(x)| = \frac{|T - T_N(x)|}{T_N(x)} \sim x^{-1/\varphi}. \tag{7}$$

Table 1. The composition x and concentration gradient Δx for the $K_2Cu_xCo_{1-x}F_4$ samples studied, estimated over distances limited by a diaphragm, for weak values of dilution. The Néel temperature, its dispersion ΔT_N, and the ratio $\Delta T_N/T_N$ due to the concentration gradient are also reported. The estimated upper value for the critical region t_M is calculated from [7] and expression (7), giving $|t_M| = 10^{-1}$ at the lower dilution $x = 0.095$.

x	Δx (mm)	T_N	ΔT_N	$\Delta T_N/T_N$	$\lvert t_M\rvert$
0.095	<0.003	97.7 K	±0.036 K	3.7×10^{-4}	10^{-1}
0.130	<0.001	93.2 K	±0.012 K	1.3×10^{-4}	4.4×10^{-2}
0.177	<0.010	88.4 K	±0.12 K	1.4×10^{-3}	1.4×10^{-2}

Values of $|t_M(x)|$ are then calculated (table 1) using a typical value for φ of 0.35 [7]. The disappearance of the λ-type anomaly does not mean a loss of long-range order; magnetization or magnetic diffuse scattering measurements can probe it above x_c [12].

Another interpretation of the critical-region narrowing caused by disorder is also possible from a theory developed recently for disordered 2d Ising systems [20]; a new intermediate phase is expected to appear between the antiferromagnetic and the paramagnetic phases, which breaks the usual logarithmic divergence of the specific heat below a reduced temperature t_c which depends strongly upon mixing:

$$t_c = \frac{|T_C - T_N|}{T_N} \exp(-c_1/g). \tag{8}$$

The strength of the random-bond fluctuations g increases markedly with the impurity concentration x; for example, for a mixed magnetic system one obtains $g = 0.34(1-x)(1-2x)^{-2}$ [20]. Using this estimation for g and the constant value $c_1 = 0.53$, as determined in [20], we found $t_c = 8 \times 10^{-2}, 6 \times 10^{-3}, 1.5 \times 10^{-3}$ and

2×10^{-5} for samples with compositions $x = 0.2, 0.177, 0.13$ and 0.095, respectively. The smearing of the critical region ($t \sim 10^{-1}$) clearly occurs down to $x_c \sim 0.2$.

Finite-size effects in computer simulations may cover the details of the critical properties. For instance, estimations of these effects [20] indicate that the narrow intermediate phase cannot be seen in systems studied in Monte Carlo simulations [21].

Up to now, the variation of the Schottky anomaly with dilution had never been tested from direct specific heat measurements in 2d Ising disordered compounds [2]. From our LB data (figure 2(b)) we checked that its magnitude scales with x^2 ($0.2 < x < 0.58$), the probability of finding two nearest-neighbour sites occupied by Co ions, in agreement with expression (2). For $x_c < x < x_p$ the Schottky anomaly arises from clusters of coupled 2d Ising spins; it ought to be at its maximum at a temperature $T_m = 0.83|J_{Co-Co}|$. Starting from the experimental value $T_m = 72$ K, measured for the sample with $x = 0.31$, we deduce $|J_{Co-Co}| = 89 \pm 4$ K, in good agreement with previous determinations of this exchange integral. As is well known [19], at the Co–Co magnetic percolation threshold ($x \sim x_p = 0.5$) the effective 1d Ising character of macrobonds gives rise to a broader Schottky anomaly (figure 2(b)).

In $K_2Cu_xCo_{1-x}F_4$ the variation of T_N with x at small Cu dilution (table 1), $d(T_N(x)/T_N(0))/dx \sim -1.20 \pm 0.05$, agrees well with its previous determination from susceptibility measurements [12]. This system differs significantly from the dilute case with diamagnetic ions, such as for $K_2Mg_xCo_{1-x}F_4$, for which this quantity reaches -1.95 [2]. Our value is closer to results of calculations for random-bond 2d square lattices [22]. In particular, this value of -1.20 can be determined for a random-bond system with only two exchange integrals J_1 and J_2 with $J_1/J_2 \sim -0.1$. The dilution at percolation, $x_p = 0.5$, is also much more consistent with the random-bond case, in contrast to the usual random-site situation [19], for which $x_p = 0.41$.

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