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The dynamic signature of highly anisotropic correlation near the phase transition in $KCaF_3$

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Abstract. In the framework of the structural instability studies in the archetype perovskite compounds, the unusual mechanism of phase transition occurring in potassium calcium fluoride $KCaF_3$, due to both condensation of $R(0.5, 0.5, 0.5)$ and $M(0.5, 0.5, 0)$ points of the first cubic Brillouin zone, was investigated by inelastic neutron scattering. The appearance of a central component, and evidence of the softening of the whole phonon branch $(0.5, 0.5, \xi)$ of the reciprocal space, is displayed and discussed in the framework of theoretical models, which take into account the strong anisotropy of the coupling constants driving the in-plane or the plane-to-plane CaF_6 octahedron rotations around the [001] cubic axis. Furthermore the behaviour of the soft modes, responsible for the transition versus temperature, seems to indicate that an intermediate disordered phase with cubic average symmetry can be introduced in such systems. The basis of an original model describing this structural phase transition, where rotations of rigid octahedra are symbolized by pseudo-spins, is proposed.

1. Introduction

In the framework of understanding structural phase transitions, highly anisotropic systems are of special interest because they can involve not only a well $\boldsymbol{q}$ localized soft mode but an extended region of instability in the Brillouin zone. This situation was fully analysed theoretically by Kerr and Bishop [1] in a system of weakly coupled chains with strong interactions within each chain. This anisotropy is clearly realized in structures made of rigid units such as the octahedra in perovskites. In these compounds, when looking at the phonon modes whose eigenvectors are octahedra rotations around [001] axis, it appears that in-plane coupling is very strong whereas plane-to-plane coupling is very small. As previously discussed by Rousseau *et al* [2], this anisotropy is characterized by the dispersion of the T_2 and T_5 phonon branches of the R–M line $(0.5, 0.5, 0.5 - \eta)$ near the R_{25} mode ($\eta = 0$). Lattice dynamics calculations show that T_2 modes correspond to rotations of undistorted octahedra around the c axis, nearly unaffected by the phase shift introduced with a non-zero value of η. On the other hand, the twofold degenerate T_5 modes (octahedron rotations around a and b cubic axes) involve more and more octahedron deformations as η increases. Following Gesi *et al* [3], for $\boldsymbol{q}$ vectors $(0.5, 0.5, 0.5 - \eta)$, the dispersion near the R_{25} mode may be defined by

$$\omega^2 \begin{pmatrix} \eta \\ T_2 \end{pmatrix} = \omega^2_{R_{25}} + \lambda_1 |\eta|^2 \qquad \omega^2 \begin{pmatrix} \eta \\ T_5 \end{pmatrix} = \omega^2_{R_{25}} + \lambda_2 |\eta|^2$$

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showing that coupling anisotropy may be estimated quantitatively by the ratio λ_2/λ_1. As summarized by Rousseau *et al* [2], $\lambda_2/\lambda_1 \approx 70$ in AMF_3 fluroperovskites such as $KMnF_3$ and $RbCaF_3$ whereas λ_2/λ_1 is much smaller in $SrTiO_3$ (10.6 according to Gesi *et al* [3] or 25.5 according to Stirling [4]). In order to test the model of Kerr and Bishop [1], we looked for systems more anisotropic than $KMnF_3$ and $RbCaF_3$ suitable for neutron scattering experiments. In AMF_3 fluoroperovskite compounds, it appears that the highest anisotropy is realized with the compound $KCaF_3$ because the highest-temperature phase transition is due to the simultaneous condensation of both M_3^y and R_{25}^x modes which end the T_2 phonon branch. This special situation seems to be associated with a completely flat T_2 branch corresponding to $\lambda_1 \approx 0$.

In this paper, we analyse inelastic neutron scattering data recorded on $KCaF_3$. The experimental results are discussed on the basis of Kerr–Bishop simulations.

2. Experimental details

The neutron scattering experiments were performed on the 4F1 triple-axis spectrometer situated on a cold source at the LLB (Saclay, France). A Soller slit system with horizontal divergence 20′–30′–30′ was used to define the neutron path. Fixed incident neutron energy at 4.99 meV (that corresponds to $k_I = 1.553$ Å) was obtained from a pyrolytic graphite (002) monochromator. Contamination was eliminated with the use of a cooled beryllium filter. Constant-Q scans have been recorded at different points $(1.5, 0.5, \xi)$ of the R–M line in the $(3h\ h\ l)$ scattering plane.

The $KCaF_3$ single crystal used for measurements had a volume of 2 cm^3 and a rather poor mosaic spread of 1°. This sample was grown under a dry inert atmosphere (argon gas) using the Bridgmann–Stockbarger modified crystal growth technique. The starting products were high-purity powders obtained from commercial CaF_2 or previously grown KF. Growth was carried out with an adapted temperature protocol between 1360 and 1200 K at a cooling rate of 4.5 K h^{-1}. A good-quality transparent crystal block could be then extracted from the crucible.

3. Results

The temperature of the cubic-to-orthorhombic phase transition was determined by monitoring the peak intensity at the zone boundary reciprocal lattice points $(1.5, 0.5, 2.5)$ and $(1.5, 0.5, 2)$ versus the temperature through the transition. The results, shown in figure 1, confirm the simultaneous condensation of both the M_3^y and R_{25}^x modes at 558 K as previously mentioned by Bulou *et al* [5] and also by Hidaka *et al* [6] at 545 K.

The profiles of inelastic scans were analysed with a fitting procedure from B Hennion [7] which takes into account the response function (damped oscillator, Gaussian function, Lorentzian function, delta function, Bragg peak contamination, background), the shape of the dispersion curves (linear approximation) in the scattering plane and the four-dimensional resolution function $RF(\boldsymbol{q} - \boldsymbol{q}_0,\ \omega - \omega_0)$ defined from the spectrometer configuration, the mosaic spreads (monochromator, sample, analyser) and the divergences of the neutron beam. Resolution calculations showed that, in our configuration, Bragg energy width is greatly affected by the sample mosaicity, whereas the total energy projection is not affected. In our case, as the central peak is not localized on a point but on a line of the reciprocal lattice, its observed width (FWHM $\sim$ 0.075 THz) is very close to the total energy projection (FWHM = 0.070 THz) calculated at the R point. Then, so long as the spectrometer

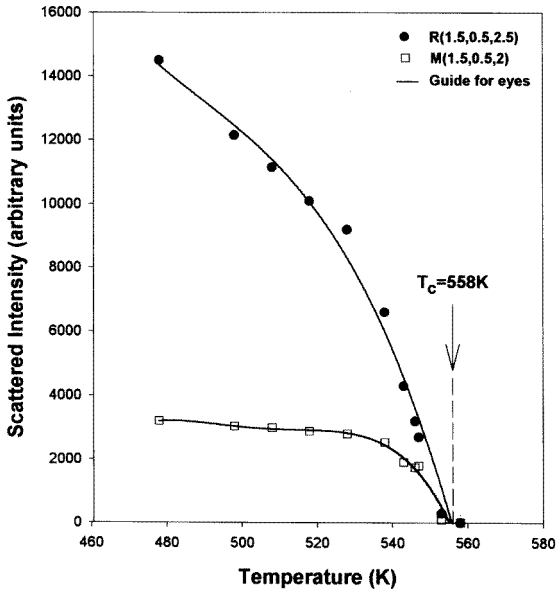

Figure 1. Intensity versus temperature at the R(1.5, 0.5, 2.5) and M(1.5, 0.5, 2) points of the first cubic Brillouin zone.

parameters are perfectly known, the poor mosaicity spread of the crystal was not a drastic handicap for the analysis of our data.

The calculated intensity $I(\boldsymbol{q}_0, \omega_0)$ is the convolution of the scattering function $S(\boldsymbol{q}, \omega)$ with the instrumental resolution function $\mathrm{RF}(\boldsymbol{q} - \boldsymbol{q}_0, \omega - \omega_0)$:

$$I(\boldsymbol{q}_0, \omega_0) = \frac{k_f}{k_i} \iint S(\boldsymbol{q}, \omega)\, \mathrm{RF}(\boldsymbol{q} - \boldsymbol{q}_0, \omega - \omega_0)\, \mathrm{d}^3 q\, \mathrm{d}\omega \tag{1}$$

where k_f and k_i are the wave-vectors of the scattered and incident neutrons. The simplest theory of the scattering from a soft mode ($\hbar\omega_0 \ll kT$) describes the scattering function by a classical damped oscillator:

$$S(\boldsymbol{q}, \omega) = \frac{kT}{\pi\hbar} |F(\boldsymbol{Q})|^2 \frac{\Gamma}{(\omega_0^2(\boldsymbol{q}, T) - \omega^2)^2 + \Gamma^2\omega^2} \tag{2}$$

where $F(\boldsymbol{Q})$ is the inelastic structure factor of the soft mode. When the mode becomes over-damped ($\omega_0 \ll \Gamma$) the scattering function reduces to the Lorentzian form:

$$S(\boldsymbol{q}, \omega) \approx \frac{kT}{\pi\hbar} \frac{P_0}{\omega^2 + \gamma^2} \qquad P_0 = |F(\boldsymbol{Q})|^2/\Gamma \qquad \gamma = \omega_0^2/\Gamma. \tag{3}$$

Energy scans were performed at M(1.5, 0.5, 0), R(1.5, 0.5, 0.5) and along the R–M line (1.5, 0.5, ξ). In order to minimize the number of adjustable parameters, both elastic incoherent scattering and background were measured at each temperature from an energy scan at (0.9, 0.3, 1.3). The eigenvectors of the phonon modes (octahedron rotations around [001] axis) being the same all along the R–M line (except at the R point where it is twice that elsewhere), the dynamical structure factor was determined from high-temperature measurements ($T - T_c > 100$ K) and fixed at its average value. Under these conditions, the scattering function given in equation (2) is defined by only two parameters: the

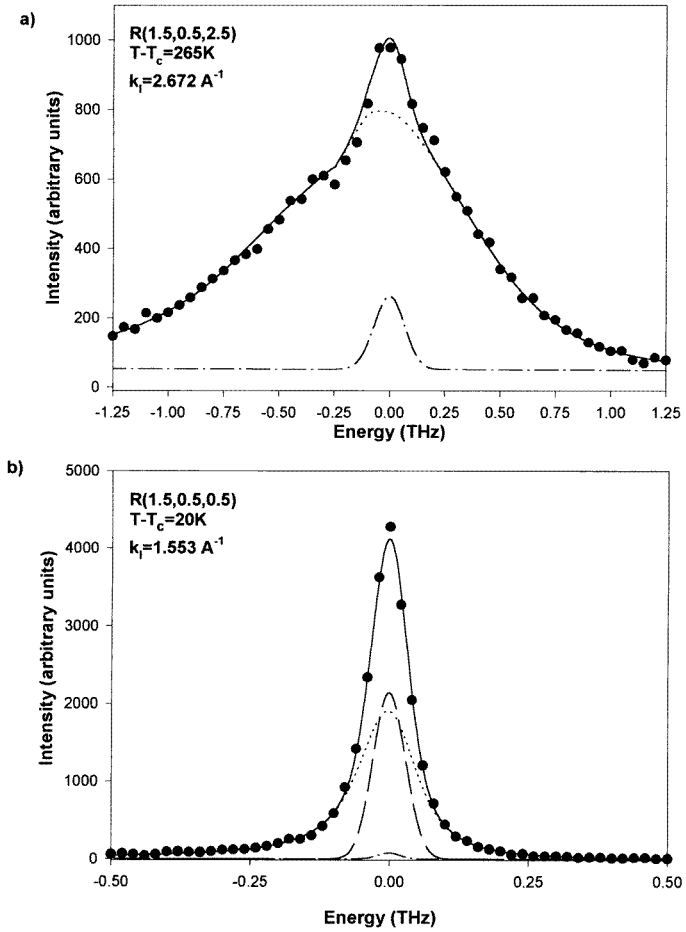

Figure 2. Energy scans at the R point of the cubic Brillouin zone for $KCaF_3$: (a) far from the transition; (b) close to transition. ● indicate experimental data; the solid line corresponds to the best fit obtained (quality factor equal to 0.96 for fit (a) and 2.28 for fit (b)), the dotted line is the over-damped oscillator contribution, the dash–dot line is the elastic incoherent scattering and the long-dot line is the central peak contribution (only observable here in (b)).

phonon frequency ω_0 and the phonon width Γ. As shown in figure 2(a), far from T_c the spectra are unambiguously interpreted by a simple over-damped oscillator ($\omega_0 = 0.76$ THz, $\Gamma = 1.4$ THz, $T - T_c = 265$ K). On the other hand, as previously mentioned by Satija and Cowley [8], when approaching T_c, analysis of the results becomes ambiguous because the spectra corrected from the measured elastic incoherent contribution can be equally well reproduced by one of the following combinations:

(a) an over-damped oscillator of fixed width ($\Gamma = 1.4$ THz) and a temperature dependent narrow Lorentzian centred on $\omega = 0$;

(b) an over-damped oscillator with a temperature dependent width;

(c) a Lorentzian with a temperature dependent width.

For example, very good fits were obtained with a drastic increase of Γ when approaching T_c ($\Gamma = 8.5$ THz, $T - T_c = 5$ K). Since a width of 8.5 THz is not physically acceptable

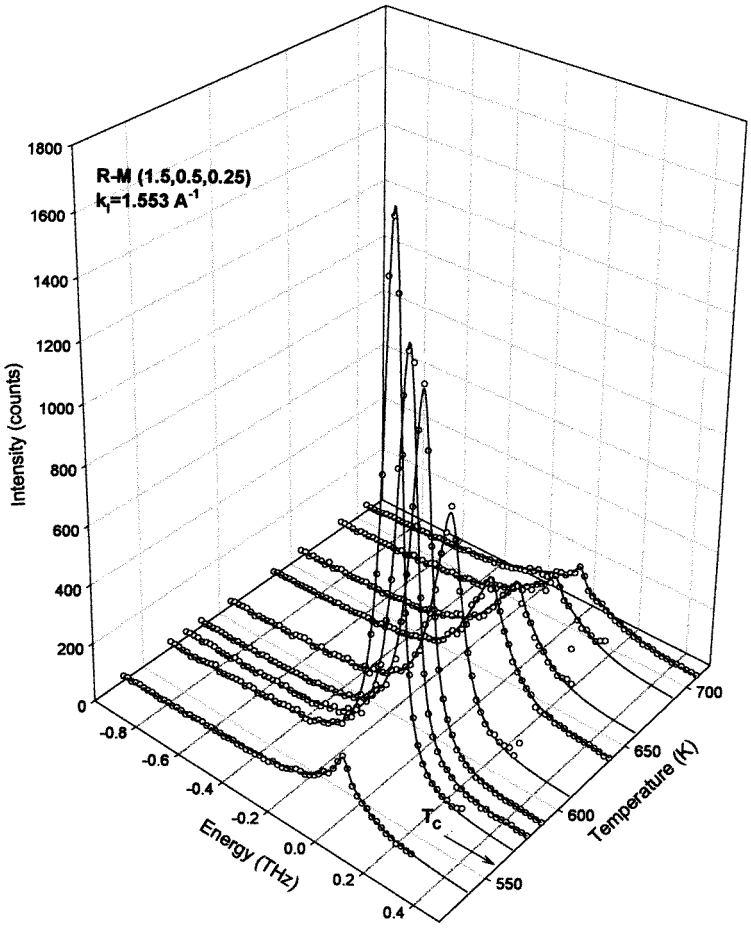

Figure 3. Constant-Q scans at the middle of the R–M line (1.5, 0.5, 0.25) of the cubic Brillouin zone. The full lines represent the fitted scans. In each fit three contributions are introduced: the phonon mode corresponding to an over-damped oscillator, the elastic incoherent scattering and close to transition the central peak contribution.

for a phonon in an ordered medium and in order to compare our results with previous work on $SrTiO_3$, $KMnF_3$ and $RbCaF_3$, we decided to hold Γ fixed at the value obtained far from T_c($\Gamma = 1.4$ THz).

Finally all the spectra were adjusted with the following scattering function:

$$S(\boldsymbol{q},\omega) = \frac{kT}{\pi\hbar}\left[A(\boldsymbol{q})\delta(\omega) + |F(\boldsymbol{Q})|^2 \frac{\Gamma}{(\omega_0^2(\boldsymbol{q},T)-\omega^2)^2+\omega^2\Gamma^2} + \frac{B(\boldsymbol{q},T)}{\omega^2+\gamma^2}\right] \tag{4}$$

where the intensity of the elastic incoherent scattering $A(\boldsymbol{q})$ is measured, the width Γ and the structure factor $|F(\boldsymbol{Q})|^2$ of the phonon contribution are fixed at the values determined at high temperature, and the width γ and the amplitude $B(\boldsymbol{q},T)$ characterize the additional central component. As γ deduced from the fits was always found to be smaller than the resolution width, the additional central component is identified as a central peak in the following. To illustrate this discussion a typical fit close to transition is displayed in figure 2(b), evidencing the presence of an intense central peak. Moreover, in figure 3, a characteristic evolution of

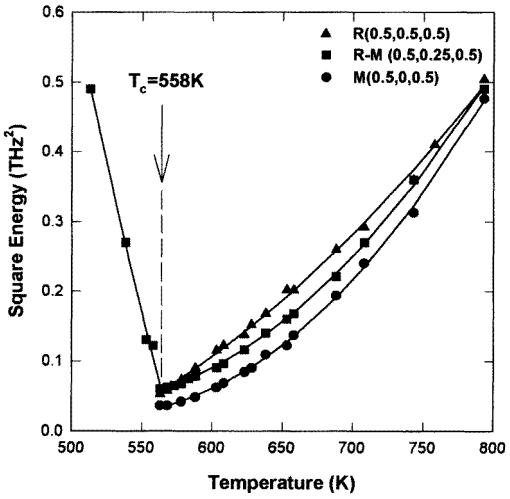

Figure 4. Evolution of the soft-mode square energy along the R–M phonon branch versus temperature.

energy scans versus temperature, fitted with the procedure previously described, is shown in the case of the $(1.5, 0.5, 0.25)$ middle point of the R–M phonon branch.

With the procedure described before, we were able to determine both the $\boldsymbol{q}$ and temperature dependences of phonon frequency ω_0 and central peak intensity $B(\boldsymbol{q}, T)$. Figure 4 shows the soft-mode behaviour observed at the R$(0.5, 0.5, 0.5)$ point, the M$(0.5, 0, 0.5)$ point and between these two points $(0.5, 0.25, 0.5)$ of the Brillouin zone. This result clearly evidences the softening of the whole T_2 branch of the R–M line in agreement with the simultaneous condensation of R_{25}^x and M_3^y modes leading to the orthorhombic phase corresponding to $a^-b^+c^0$ tilt systems in Glazer's notations [9]. Below T_c, the increase of the soft-mode frequency masked by Bragg peak intensity at R and M points is easily observed between R and M; its square frequency exhibits a linear Landau behaviour.

As predicted by Kerr and Bishop [1], the central peak occurring in the highly anisotropic system is not localized either at the M point or at the R point but is delocalized all along the R–M line (see figure 5). Below T_c the central peak observed between R and M disappears abruptly when the 3D plane-to-plane correlations are achieved. An extensive study of the Q width of this central peak as a function of Q and temperature will be presented elsewhere [10].

4. Discussion

As described before, the unusual phase transition observed in $KCaF_3$ is mainly characterized by the simultaneous condensation of both R_{25}^x and M_3^y soft phonons and the occurrence of a narrow central peak all along the R–M line. According to Kerr–Bishop [1] computer simulations, these original features can be attributed to the strong anisotropy of the coupling constants driving the in-plane or the plane-to-plane octahedra rotations around a [001] axis. Nevertheless, we do not observe the minimum of ω_0^2 at $T_s > T_c$ as predicted by Kerr and Bishop, but far from T_c the soft-mode frequency follows a Landau behaviour $\omega_0^2 \propto (T - T_s)$ as shown in figure 6 and previously reported by numerous authors (see for example the

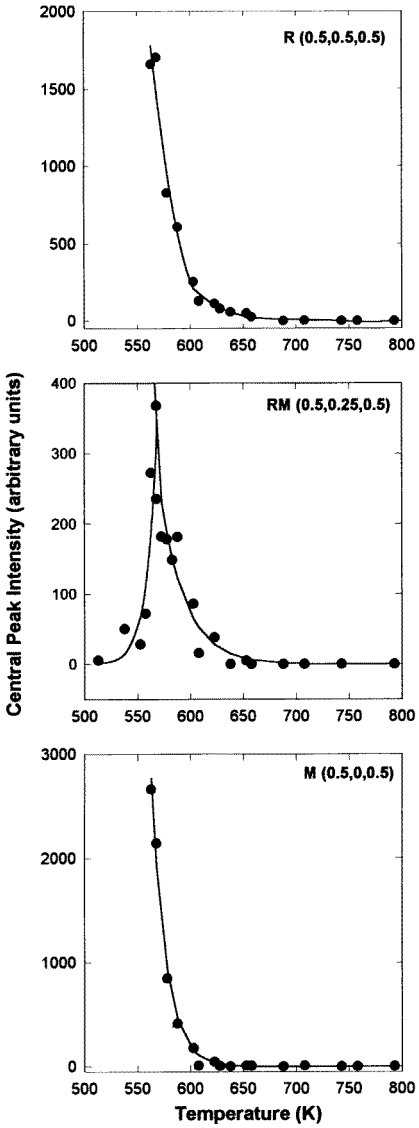

Figure 5. Central peak intensity along the R–M phonon branch versus temperature.

reviews of Cowley and Bruce [11–13] and references therein). Actually, the main problem between this theory and the experimental observations concerns the dimension of the space in which the entities interact: the Kerr–Bishop microscopic model [1] connects 1D chains instead of 2D planes in perovskite compounds.

With respect to the occurrence of two characteristic temperatures, the soft-mode temperature T_s and the critical temperature T_c, we can mention the Landau description proposed by Bulou *et al* [14], which takes into account two order parameters associated respectively with R_{25} and M_3 soft-modes. This description is not fully satisfactory because it considers only two soft-modes R_{25} and M_3 instead of the entire T_2 phonon branch, but it introduces the existence of a disordered phase between T_s and T_c. In fact our

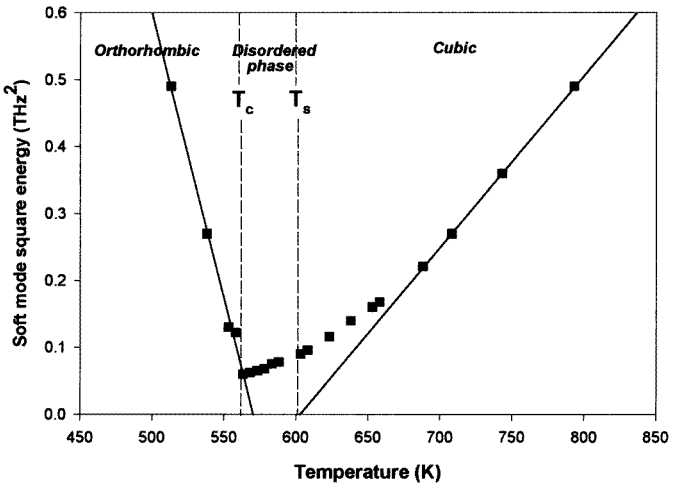

Figure 6. Linear evolution of square energy versus temperature for the soft mode of the T_2 phonon branch, located at the $(0.5, 0.25, 0.5)$ point in the cubic Brillouin zone.

experimental observations are consistent with a softening of the T_2 phonon branch which should condense at T_s and give a partly disordered phase made up of a random pile of correlated planes with a non-zero 2D order parameter (octahedron rotation angle Φ) in each plane but a zero 3D order parameter defined by $\eta(T) = C(T)\Phi(T)$ where $C(T)$ represents the correlation between the planes. When associating a pseudo-spin with the static rotation of an octahedron, one can consider that lowering the temperature gives rise to pseudo-spins induced by the condensation of the soft-mode at T_s; the 3D symmetry change observed at $T_c < T_s$ occurs when the increase of $\Phi(T)$ induces a plane-to-plane coupling large enough to realize the 3D coupling. Near T_s, 3D fluctuations involving octahedron precessions [15] prevent the complete vanishing of the soft-mode at T_s. In order to sustain this description we are studying the propagation of acoustic phonons perpendicularly to the random pile of correlated planes. First experiments [16] clearly evidence a drastic increase of energy width of these phonons as λ approaches the correlation length between adjacent planes. Further experiments are in progress.

Acknowledgments

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