Optical polarization contrast and twin-domain structure of high-temperature superconductor single crystals

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An investigation was made of the optical polarization contrast observed when twins in $YBa_2Cu_3O_{7-x}$ and $GdBa_2Cu_3O_{7-x}$ single crystals were examined in reflected light. Transmission electron microscopy was used in an analysis of the characteristics of the contrast due to the presence of narrow (i.e., thinner than the wavelength of light) twin domains. The phase shift $\Delta\varphi$ experienced by waves of different polarizations on reflection from the basal end (containing the **c** axis) faces of single crystals was determined for wide domains. The values of $\Delta\varphi$ revealed a strong anisotropy of the optical conductivity σ_{opt} characterized by preferential direction along CuO chains, supporting the quasione-dimensional nature of σ in 1-2-3 compounds.

The oxygen content of single crystals of high-temperature superconductors $RBa_2Cu_3O_{7-x}$ (R is a rare-earth element) increases in the course of slow cooling in air from the growth temperature (950–1000 °C) or when these crystals are annealed in an oxygen atmosphere at temperatures 400–500 °C. This results in filling of the 01 positions (empty at high temperatures) in Cu1 copper planes lying between barium planes. When the oxygen concentration becomes sufficiently high ($x \lesssim 0.5$) and the temperature drops below the critical value ($T_c \sim 600$ °C), the oxygen atoms become ordered forming CuO chains. This results in a transition from the tetragonal $P4/mmm$ to the orthorhombic $Pmmm$ phase.[1] This phase transition is accompanied by the appearance of a highly developed twin structure.[2,3] As demonstrated already for low-temperature superconductors, twin boundaries have a considerable influence on the anisotropy of electrical and magnetic properties,[4,5] alter the values of the critical currents and fields,[6] act as pinning centers of the Abrikosov vortices,[7,8] and even increase the superconducting transition temperature,[4,9] which is attributed to the appearance of two-dimensional superconducting structures.[4,10] Therefore, in investigations of high-temperature superconductors it is extremely important to analyze the twin structure and to study it in conjunction with electrical and magnetic properties of crystals of these superconductors.

Advanced electron-microscopic and x-ray diffraction methods have made it possible to establish the presence of twins in 1-2-3 single crystals of high-temperature superconductors and to determine the misorientation of crystallographic axes in these twins.[2,3,11] However, only small fragments of the twin domain structure can be studied in an electron microscope and it is necessary to subject a sample to a preliminary thinning, whereas x-ray diffraction gives only the average pattern in a crystal. The fullest information on the twin structure can be provided by an optical polarization method based on a change in the polarization of light due to reflection from an anisotropic medium.[12] This method has been used successfully in studies of twins in $EuBa_2Cu_3O_{7-x}$ (Refs. 13 and 14) and $YBa_2Cu_3O_{7-x}$ (Refs. 15 and 16) single crystals. We shall report more detailed features of the characteristics of the polarization contrast of twins in yttrium and gadolinium cuprates. We analyzed the nature of the contrast on the basis of direct observations of the twin structure in an electron microscope and in transmitted polarized light. We found that an optical microscope can be used to study not only topological details of the twin structure, but also to determine reliably the directions of the crystallographic axes **a** and **b** in twins. Measurements of the phase shifts experienced by waves of different polarizations and studies of the linear dichroism (in transmitted light) were used to determine the optical conductivity anisotropy included in Ref. 15, which could be regarded as evidence of quasi-one-dimensional conduction (along CuO chains) in 1-2-3 crystals of high-temperature superconductors predicted by energy band calculations.[17]

RESULTS AND DISCUSSION

We investigated $YBa_2Cu_3O_{7-x}$ and $GdBa_2Cu_3O_{7-x}$ single crystals grown from a nonstoichiometric molten mixture of Y_2O_3, Gd_2O_3, BaO_2, and CuO oxides by slow cooling in the range 1100–900 °C in air. These crystals were platelets with a highly developed basal plane; they were ~ 20 μm thick with typical dimensions of 1×1 mm in the plane of a platelet. Such crystals were placed in a polarizing microscope without any preliminary treatment and were investigated using crossed Polaroids and normally reflected light.

If a surface under investigation is anisotropic, the components of a light wave polarized along the principal optic axes of a crystal could acquire different phase shifts as a result of reflection. Then, an initially linearly polarized wave should become elliptically polarized as a result of reflection and transmission should be observed in crossed Polaroids. The effect should be maximal when the principal optic axes of a crystal are oriented along the diagonal between the directions of polarization of the Polaroids, but there should be no transmission if the principal axes lie along these polarization directions. Consequently, the intensity of the transmitted light should vary when a crystal is rotated about the microscope axis and should be repeated every 90°.

A typical pattern observed for the (001) basal plane of $YBa_2Cu_3O_{7-x}$ was in the form of two systems of fringes oriented along the [110] and [1$\bar{1}$0] directions, which became darker and disappeared when the fringes were oriented

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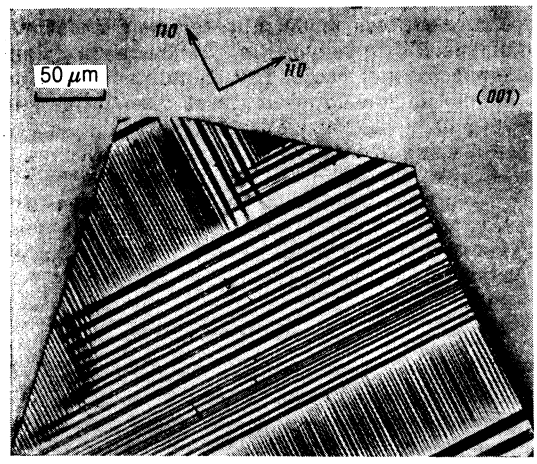

FIG. 1. Optical polarization contrast of twins in $YBa_2Cu_3O_{7-x}$ illuminated with normally reflected light.

at 45° to the polarizers. The pattern was repeated completely when the sample was rotated by $n \times 90°$ about the light beam axis. Introduction of an additional path difference (by a compensator) into the incident or reflected beam caused the neighboring domains to become differently colored[1)] and the contrast was reversed by rotation through 90° (Fig. 1), but it was restored after rotation through 180°. These results indicated the optic axes in the domains were oriented at 45° to the boundaries and were mutually perpendicular in the neighboring domains. It was therefore natural to assume that the optic axes were oriented along the **a** and **b** crystallographic axes and the observed pattern represented a twin domain structure.

We checked whether the polarization contrast was related to optically unresolved twin superstructures: this was done using an electron microscope producing a direct (transmission) image and employing microdiffraction in the case of chemically thinned parts of samples which should "inherit" the domains revealed in the reflected light. This experiment confirmed that the contrast was associated with the rotation of the **a** and **b** axes in the twins and not due to the presence of additional structure defects in the twins.

These results were obtained when the twin domains were sufficiently wide. However, the recorded images included also fairly narrow ($< 1\,\mu$m) fringes in which the color changed little and which always remained dark against the background of the wider domains when a sample was rotated about the microscope axis (Fig. 2a). We were able to compare directly the optical contrast of such fringes with the electron-microscopic contrast. It is clear from Fig. 2b that the narrow fringes represented separate twin spacers of width less than the optical wavelength λ. Clearly, in this case the optical contrast was determined not so much by a change in the polarization of light on reflection as by the diffraction effects. It should be pointed out that our optical experiments revealed twin spacers in a fairly wide homogeneous region even when their width was considerably less than λ (we observed twins which were 0.01 μm wide, according to the electron-microscopic data, but their images were smeared out to $\sim 0.3\,\mu$m and were characterized by a weak contrast).

In the basal plane we also observed regions of weak contrast with poorly resolved fine fringes (Fig. 3a), which changed only slightly as a result of rotation of the sample. An electron-microscopic investigation showed that these regions were characterized by a high density of twins of width much less than the wavelength of light (Fig. 3b). When the dimensions of the alternate twins were the same, there was practically no optical polarization contrast. When the domains of one of the types (for example, those with a given direction of the **a** axis) were wider than the domains of the other type (this was clearly due to the action, at the moment of transition from the tetragonal to the orthogonal phase, of internal stresses imposing the observed orientation along the **a** axis), an average contrast was observed. This contrast was less than for a single wide domain, but it did not change on rotation of the sample, as in the case of homogeneous orthorhombic samples. Therefore, even when twins were not revealed at optical resolution, we could determine whether the crystal in question was in the orthorhombic phase and whether it contained twins: this could be done by analyzing the polarization contrast if the domains had different dimensions.

In the case of the fine equal-width domains the intensity of the light reflected from the basal plane (observed in crossed polarizers) was minimal and was not affected by rotation of the sample. A similar situation was observed in the case of samples of the tetragonal phase prepared by annealing in vacuum. A tetragonal crystal could be distinguished from an orthorhombic crystal with a high density of twins by x-ray diffraction or electron-microscopic investigations. However, in practice, even crystals with a high twin density always contained regions with an inhomogeneous domain structure where the contrast was observed and this made it possible to determine whether the crystal was orthorhombic.

A comparison of the small-scale patterns of the twin domain structure obtained by electron microscopy in the optically revealed large domain configurations demonstrated that the domain structure topology did not differ from the topology of macroscopic domains. Hence, the relationships governing the formation of the twin structure were the same

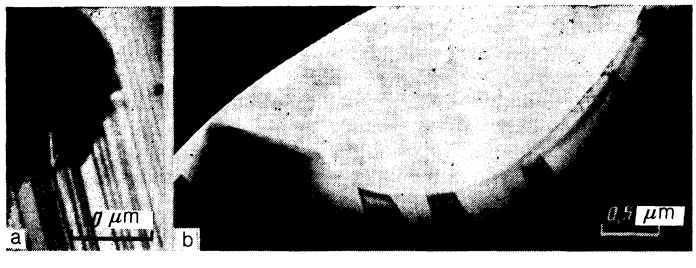

FIG. 2. Narrow twin spacers: a) observed using polarized light (normal reflection); b) observed in an electron microscope (by transmission). The arrow in Fig. 2a identifies the region where the electron micrograph of Fig. 2b was recorded.

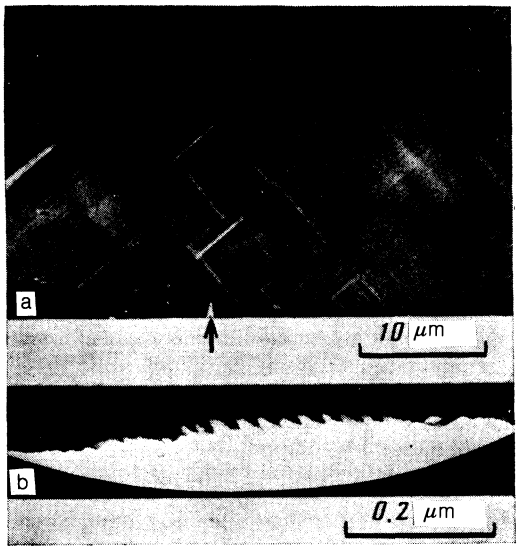

FIG. 3. a) Optical contrast in the case of a high density of narrow twin domains. b) Electron micrograph of the twin pattern in the region identified by the arrow in Fig. 3a.

at the microscopic level and could be investigated only by the optical polarization method. These domain structure details were observed also for $GdBa_2Cu_3O_{7-x}$, but the optical contrast of the domains in the latter crystals was weaker than in $YBa_2Cu_3O_{7-x}$.

Twin domains were observed also on the ends of the investigated single crystals. Figure 4 shows the domain structure pattern on a (010) face. In this case the domain boundaries were oriented approximately along the **c** axis, whereas the **a** and **b** axes were in the plane of the face and oriented alternately along the normal direction in the neighboring domains. The following is worth noting: in the basal plane the domain boundaries were straight and converged to a wedge only near the ends of the twins terminating inside a crystal, whereas along the **c** axis the domains were noticeably bent. This was evidence of a significant anisotropy of the surface energy of twin boundaries. An analysis of the images of twins on the end faces revealed the most surprising result. It was found that when a sample was rotated, the contrast changed only in the case of domains of the same type and it was repeated every 90°, whereas the neighboring domains remained constantly dark. We therefore concluded that in the case of light polarized along the **c** axis the phase shift on reflection was the same as in the case of polarization along one of the basal-plane axes.

A Berek compensator was used to determine the difference between the phases in the neighboring domains on an (010) face. In the case of some domains (called *a'c* domains because the **a'** and **b'** optic axes were linked to the **a** and **b** crystal axes, leaving the sign of the orientation indefinite, and because the surfaces of these domains were parallel to the **a'** and **c'** axes) we found that $\Delta\varphi_{a'c} = 15.3° \pm 1.5°$ (which was true of $YBa_2Cu_3O_{7-x}$), whereas in the case of other (*b'c* domains) we obtained $\Delta\varphi_{b'c} = 0 \pm 1.5°$ (the wavelength of light was $\lambda = 546$ nm). The phase of the light polarized along **a'** was delayed relative to the light with the **c** polarization. Similar changes in the phase shift in the basal plane gave rise to $\Delta\varphi_{a'b'} = 14.0 \pm 1.5°$, which agreed within the limits of the experimental error with $\Delta\varphi_{a'c}$ (in agreement with $\Delta\varphi_{b'c} \approx 0$). In the case of $GdBa_2Cu_3O_{7-x}$ single crystals the values were somewhat less: $\Delta\varphi_{ab} = 8.0 \pm 1.5°$. A value of $\Delta\varphi_{ab}$ of the same order of magnitude ($\sim 30°$) was reported in Ref. 14 for europium cuprate. However, the absolute values of the phase shift were unimportant, because they depended on the oxygen content and they could be altered greatly by annealing.

A more interesting result was the anisotropy of $\Delta\varphi$ observed on the end faces. They allowed us to draw important conclusions on the nature of conduction in the investigated single crystals. In fact, the phase shift in the case of normal reflection is determined by the absorption coefficient (k_i) and the refractive index (n_i) of light of the given (*i*-th) polarization. When light is polarized along the principal optic axes, we have[18]

$$\varphi_i = \operatorname{arctg} \frac{2k_i}{n_i^2 + k_i^2 - 1}. \qquad (1)$$

An analysis of Eq. (1) shows that the most probable values of the phase shifts corresponding to the measured differences $\Delta\varphi_{ij} = \varphi_i - \varphi_j$ should be $\varphi_c \sim \varphi_{b'} \sim 0$ and $\varphi_{a'} \sim 14°$.[2)] (Moreover, the values of $\varphi_{b'}$ and φ_c may be equal and different from zero if $k_{b'} \neq k_c$ and $n_{b'} \neq n_c$, but such degeneracy is less likely.) Then, the values of k_i for the waves polarized along the **c** and **b'** axes are close to zero, whereas the absorption coefficient for the **a'** polarization is much greater.

This conclusion is supported by direct observations of the anisotropy of the absorption of light in single crystals thinned by a chemical method. The twin structure was revealed by transmission of polarized light in the absence of an analyzer. In suitable domains the light with the **b'** polarization passed through a crystal whereas in the **a'** polarization the domains were nearly opaque.

Further support for the difference between $k_{a'}$ and $k_{b'}$

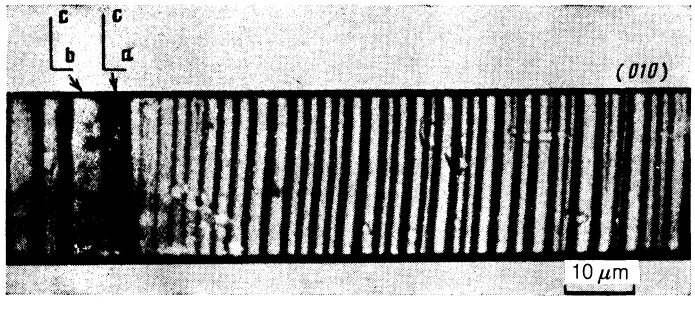

FIG. 4. Image of twin domains on the end face of a $YBa_2Cu_3O_{7-x}$ single crystal obtained using reflected polarized light.

was provided by a difference between the reflection coefficients of light polarized along the **a**′ and **b**′ axes. This was mainfested by a difference between the densities of the images of neighboring domains observed in the reflected light in the absence of an analyzer Polaroid. The domains for which the polarization of the incident wave was parallel to **b**′ were darker, in full agreement with the familiar expression for the reflection coefficient

$$R=\frac{(n_i-1)^2+k_i^2}{(n_i+1)^2+k_i^2}.$$

If $k<1$ and $n>1$ (which are the values found using unpolarized light[19]), the higher absorption coefficients k correspond to higher values R.

In our case the meaning of the inequality $k_{a'} \gg k_{b'} \sim k_c$ could be explained by recalling that the values of n and k were related to the permittivity ε of a sample and its conductivity σ at the frequency of light ν by the following expressions[18]

$$n^2=\tfrac{1}{2}((\varepsilon^2+4(\sigma/\nu)^2)^{1/2}+\varepsilon), \quad (2)$$

$$k^2=\tfrac{1}{2}((\varepsilon^2+4(\sigma/\nu)^2)^{1/2}-\varepsilon). \quad (3)$$

Assuming that the values of n and k did not differ too greatly from those deduced from the measured reflection coefficient of unpolarized light (as pointed out above, we would expect $n>1$ and $k<1$), we could assume that $\varepsilon \gtrsim 1$ and $\varepsilon \gtrsim 2\sigma/\nu$. It then follows from Eq. (3) that the different values of k for different polarizations of light should be governed mainly by the differences between the conductivity. A significant influence of the conductivity on the absorption coefficient was supported by the dependence of the phase shift due to reflection on the wavelength of light. It is clear from Fig. 5 that an increase in $\Delta\varphi$ with λ in the case of $YBa_2Cu_3O_{7-x}$ could readily correspond to an increase in σ/ν. On the whole, the values of $\Delta\varphi$ were obtained in a fairly narrow range of wavelengths of visible light. Therefore, a more rigorous interpretation would require widening of this range and in particular determination of the plasma frequency ω_p for our samples. Clearly, the proximity to ω_p could be responsible for the nonmonotonic dependence $\Delta\varphi(\lambda)$ in the case of $CdBa_2Cu_3O_{7-x}$ (denoted by Δ in Fig. 5), although there was a tendency for $\Delta\varphi$ to increase with λ. Bearing in mind this point, we would expect the conductivity along **a**′ to be considerably higher than σ along the **b**′ and c axes. Precisely this type of quasi-one-dimensional conduction in 1-2-3 cuprates was predicted by the energy band calculations[17] showing that in the orthorhombic phase the highest σ should be observed along CuO chains. However, a confirmation that the observed anisotropy of σ agreed with the theory of Ref. 17 would require more precise linking of the **a**′ and **b**′ axes to the basal axes **a** and **b** of the crystal (the CuO chains are oriented along the latter axis). This could be done on the basis of experiments involving the application of elastic stresses to a twin structure. Uniaxial stresses lowered the energy of one of the equivalent phases and increased the energy of another phase, favoring the growth of the domains of the former at the expense of the domains of the latter phase. Clearly, elongation along the [100] axis favored the growth of domains in which the longer **b** axis was parallel to the direction of elongation; conversely, it should reduce the width of the domains characterized by **a**‖[100]. A similar analysis carried out in Ref. 13 indicated that an introduction of thermoelastic inhomogeneous stresses (by local heating) gave rise to a configuration with **a**′‖**b** and **b**′‖**a**.

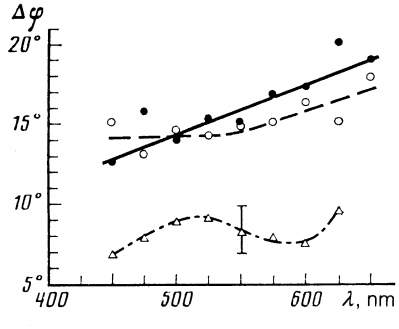

FIG. 5. Wavelength dependence of the phase shift $\Delta\varphi_{ab}$ due to reflection from the basal plane of $YBa_2Cu_3O_{7-x}$ (● and ○ represent samples belonging to different batches) and $GdBa_2Cu_3O_{7-x}$ (△) single crystals.

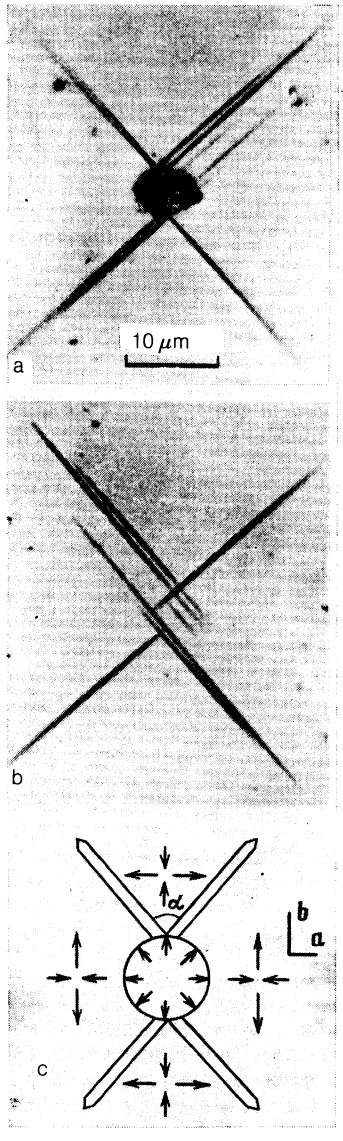

FIG. 6. a) Appearance of twin domains around a laser damage region. b) Appearance of twins on the opposite surface of a crystal. c) Schematic representation of stresses around a laser "indentation."

A different experiment utilizing a focused laser beam is illustrated in Fig. 6. Interaction between laser radiation and a homogeneous part of a crystal resulted in irreversible expansion of the lattice (because of reduction in the oxygen content in the irradiated layer), so that stresses appeared around a laser "indentation," as shown in Fig. 6c. In those regions where the **a** axis was parallel to the direction of elongation we would expect initiation of domains with the **b** axis parallel to this direction. Depending on the orientation of the axes of the original phase, a pair of points of nucleation of twins of the second phase should be located (as shown in Fig. 6c) on one of the two mutually perpendicular diameters of a laser "indentation." This analysis confirmed that $\mathbf{a}' \| \mathbf{b}$ and $\mathbf{b}' \| \mathbf{a}$.

Another interesting result, which could be used to determine the ratio of the parameters **a** and **b**, is illustrated in Fig. 6. The angle α between the "rays" of the twins created at the edges of the damage zone differed slightly from the right-angle. Measurements gave $\alpha = 89.0 \pm 0.1°$. This confirmed the conclusions reached in earlier experiments that the longer **b** axis (along which the phase of the light wave was delayed) was oriented vertically in this figure and the shorter **a** axis was horizontal. Since the twin boundaries were oriented along the diagonals of rectangles with the sides a and b, the angle α yielded the ratio $b/a = 1.016 \pm 0.002$. This was in agreement with the values reported for the investigated crystals[1]: $a = 3.825$ and $b = 3.883$ Å ($b/a = 1.015$).

Therefore, the optical polarization method (faster than any other methods for the investigation of twins) not only enabled us to analyze the twin-domain structure, but also to determine the orientations of the crystallographic axes in the individual domains of single crystals of 1-2-3 high-temperature superconductors.

In turn, such an investigation of the optical contrast in single-phase regions demonstrated that the optical conductivity was quasi-one-dimensional, which could be regarded as a confirmation of the theoretical predictions[17] of preferential conduction along the CuO chains in rare-earth cuprates. However, a rigorous confirmation of this hypothesis would require an extension of optical polarization investigations to the infrared range where the optical properties of crystals are determined by free carriers and it is possible to obtain specific information on the nature of dc conduction.

We shall conclude by noting that the observed anisotropy of σ makes it desirable to carry out detailed investigations of the configuration of twin complexes and of the structure of twin boundaries in high-temperature superconductor crystals in connection with the topology of the current paths and internal current contacts. This role of the twins is in our case more important than the usually discussed effects of twins on the characteristics of the superconducting phase transition.[4]

[1)] The appearance of color was associated with dispersion of the phase shift (for which the results of measurements are given below). Superposition of an additional phase shift in the compensator and of the phase shift (advance) due to reflection, characterized by opposite signs for the neighboring domains (so that the total phase had different values), resulted in different colors of the domains.

[2)] Naturally, φ_i should be measured from the value of π representing the phase shift on reflection from an insulator characterized by $n > 1$.

[3)] This was demonstrated recently in a more rigorous manner by comparing the direct x-ray diffraction data, obtained by I. M. Shmyt'ko for a large region free of twins in a $YBa_2Cu_3O_{7-x}$ crystal, with the optical polarization pattern of this crystal.

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