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The optical Character of the Orthorhombic Principal Planes of YBa$_2$Cu$_3$O$_{7-\delta}$ in visible Reflected Light

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To Max Berek, pioneer of ellipsometry by reflected polarized-light microscopy

Introduction

A nearly rectangular crystal plate of twinned, orthorhombic YBCO with mostly idiomorphic low index growth faces of (001)-pinacoids, (100)-and (010)-prisms was prepared for optical investigations in the visible, polarized and reflected light. It belongs to series of typical tiny plates of orthorhombic crystals which were found on the surface of a solidified flux and thus had apparently formed under reduced stress conditions [1]. One of these YBCO crystals contained a relatively large triangular single domain, which has been studied in detail in this work (Fig. 1a). The crystal plate was mounted on a spindle stage of a polarized-light microscope (Leitz ORTHOPLAN-POL) to allow a precise positioning of the object.

The optical orientation of the domain depends on the reference system of the microscope. For the following experiments the uniradial reflectivities of the crystal $R_a$, $R_b$, $R_c$ are always aligned parallel to the diagonals 1 and 2, which divide the crossed polars by 45° (Fig. 1b). In accordance with the orthorhombic symmetry $R_a$, $R_b$ and $R_c$ are in line with the crystallographic axis $a$, $b$, and $c$.

The optical properties of the morphologically dominating (001) face are described elsewhere [16] and there seems evidence that almost $R_a > R_c$. As for the optical symmetry planes on (100) and (010) the discussion of anisotropy in the visible does not go into detail and informations about elliptical vibration constants are scarcely added. The published values need to be completed, but till now it is difficult to get crystal faces which are useful for optical measurements in the visible. Relics of flux and mostly unknown microinhomogeneities often disturb specular reflection on (100)- and (010)-prism faces. That is why an optical coupling of immersion-oil between crystal surface and objective of the microscope was adopted to diminish those effects. Immersion-oil improves bireflectance and anisotropy contrast at crossed polars and suppresses the influence of scattering and absorption in transparent layers of flux and hydrates. This demonstrates the phase difference $\delta_{01}$ between $R_a$, $R_c$ on the (001)-face, which depends clearly from the refractive index $n_0$ of the optical coupling medium (normally air or, in this case, immersion-oil with $n = 1.52$) [20], [22].

Optical criterion of single- and polydomains

A measurement describing the optical properties of an anisotropic crystal face must ensure that there is no superposing influence of mimetic twinning or other misleading intergrowth. Furthermore, when executing reflectivity and ellipsometric measurements by means of a polarized-light microscope, a series of particular precautions concerning parasitic images, glare effects etc. (see at ref. 10, chapter 12) has to be respected. In case of the above mentioned single domain (Fig. 1a) it has been insured both on (001)-, (010)- and (100)-faces, that the field stop of the microphotometer (Leitz MPV1), was placed far enough away from differently oriented domains and flux nodules. Colour plate 2a, b and Figure 2a, b show the (001)-face of the triangular single domain of Figure 1a at a higher magnification with some more details. The single domain is limited by [100]-walls traversing the whole thickness of the crystal and by the right angled edges along [100] and [010], forming a nearly isosceles triangle in the (001)-plane. Inserting the Laves-Ernst-compensator creates uniform compensation colours as a sign of optical homogeneity [21]: i.e. for $Z//P$, $\sgn(\sigma) = -1$ we find a typical orange-yellow subtraction colour over the whole triangle. $Z//P$ means: in start position the angle $\sigma$ of the Laves-Ernst-compensator is zero and the higher index, $n$, of the $\lambda$-plate (first order red) runs parallel to the vibration direction of the polarizer $P$. For more details see at ref. [7] and [8].

From the instructions for use of the Laves-Ernst-compensator [7], [8], the sign of the phase difference $\delta_{01} = \delta_1$, $\delta_2$ expressed by $\sgn(K_2-K_1)$ with $K = -\arctan(\delta)$ and its correlation with the crystallographic axis is determined:
Crystal Single Domains

Fig. 1a: Crystal plate of orthorhombic YBCO; objective: 3.2x/N.A. = 0.12/nb; crossed polarizers (N); bottom right hand, marked by ▼: triangle of a single domain reflecting with a maximum of intensity in diagonal position: R₁ //1, R₂ //2, Pol //[(110)]

Fig. 1b: Orientation of the uniradial reflectivities R₁, R₂ of the triangle single domain in figure 1a; corresponding to the reference system of polarizer P, analyzer A and diagonals 1, 2 of the microscope.

e.g. for the (a, b)-plane Kₐ<Kₐ and Kₐ<Kₐ. The indices 1 and 2 refer to the fixed reference system of the microscope (see colour plate 1 and 2). The observed correspondence of the traces of the domain walls on the (001) and (001) surfaces together with the narrow transition width of T₀ of crystals of the same batch indicates that the platelet is entirely orthorhombic and rather homogeneous throughout the thickness [17].

A quantitative characterisation of the single domain areas appearing optically homogeneous consists in the measurement of orientation and form of the vibration ellipse of the reflected polarized light. The polarizers are crossed at monochromatic light and the uniradial reflectivities R₁, R₂ are set in the diagonal position as shown in Figure 2a. Then the phase-difference δ₁₂ is cancelled out by means of a tilting compensator (here: a plate of MgF₂, 4 orders, n₁ //2, Leica-Wetzlar, Germany). Moving the analyzer from the crossed position (φ₀ = 90° = N) by Δφ₀, the linearly polarized vibration extinguishes, the single domain area becomes dark and fades away in the isotropic background (Fig. 2b).

Figure 3 shows the corresponding vibration ellipse and

Fig. 2a,b: Single domain of Fig. 1a at higher magnification and same area as shown in colour plate 2b; objective: 50x/N.A. = 0.85/immersion; monochromatic light, λ = 480 nm.

2a: Crossed polarizers (N); no compensator inserted; R₁, R₂ in diagonal position; all domains on (001) show a maximum of intensity comparable to colour plate 1a.

2b: Idem Fig. 2a, but tilting compensator inserted; the elliptical vibration is converted into a linear one, which is extinguished after moving the analyzer-angle φ₀ from N (φ₀ = 90°) to φ₀ = 97° (see Fig. 3).
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the optical reference system of the microscope:
The ratio of the sides of the rectangle circumscribing the vibration ellipse corresponds to the ratio of the square root of the uniaxial reflectivities $\sqrt{R/R_0}$, (compare also the vibration ellipses of Figures 9a, 9b and 13). The parameters of the vibration ellipse refer to Berek's fundamental experiments of microellipsometry from 1937 [19]: The azimuth $\eta$ between the plane of analyzer $P$ and the semimajor axis of the vibration ellipse; the ellipticity $\Theta$, where $\tan \Theta = b/a$; $\chi = \arctan \sqrt{R/R_0}$; and $\Delta\Theta$: rotation of the analyzer from the position of crossed polarizers (N°) to the position of extinction of the linearly polarized vibration, obtained after compensation.

**Anisotropy of (100)- and (010)-faces**

As a consequence of the usually plate-like habit of YBCO crystals, the pseudotetragonal prism faces (100) and (010) are rather narrow grown along [001]. By mounting the crystal on a spindle stage, accurate perpendicular specular reflection was achieved by rotating the crystal around [100]- and [010]-zones. A zone stands for a direction of the cutting edge between two crystal faces, whose terms are enclosed by brackets like [uvw]. The prism faces usually show a simple domain pattern: mostly parallel stripes of alternately changing (a,c) = (010)- and (b,c) = (100)-domains [2], [6], [9]. In case of a very high density of [110]-walls the stripes are not resolved and a single domain is mimicked. Measurements of reflectivity on these domains are difficult to perform, especially in air, because impurities like flux nodules, which prevent an undisturbed reflection from the crystal surface, seem to stick more frequently to (100)- and (010)- than on (001)-faces. Intensities of the reflected light by adjusting the crystallographic axis a,c and b,c successively parallel to the polarizer are only given in arbitrary units [3].

The use of immersion-oil as a coupling medium between crystal and objective diminishes the influence of surface impurities on the reflectance of the crystal face, which is given by the structure and chemical composition of YBCO. Figure 4 shows the reflectivity in % as a function of wavelength, calibrated by means of a SIC- and a glass prism-standard (Leica Wetzlar). Curves 1 and 2 represent the measurements in air, curves 3-15 measured in immersion-oil; indices a, b, c refer to the uniaxial reflectivities parallel [100], [010] and [001] respectively; curve 1: $R_1$(air), curve 2: $R_2$(air), curve 3-6: $R_3$(oil), curve 7-10: $R_4$(oil), curve 11-15: $R_5$(oil).

Figures 5 and 6 show the ratio $R/R_1$, determined by photomultiplier current. The measurements on (100) and (010) are only made in immersion-oil (Fig. 5), the measurements on (001) enable a comparison of $R/R_1$, determined in air and oil (Fig. 6). The enhancement of $R/R_1$ between blue and red after changing the coupling medium from air to oil points to the increasing birefringence in immersion-oil:

$R/R_1$ on (100) $> R_2/R_1$ on (001) $> R_3/R_1$ on (100). $R_1/R_2$ and $R_1/R_3$ increase, $R_1/R_4$ decreases from blue to red. Compared with immersion-oil, these tendencies are less noticeable in air.

Further informations are given at crossed polars by use of the Laue-Enst-compensator (see colour plate 1a-f and 2a,b). In colour plate 1a-f the (100)- and (010)-prism faces are folded along the [010]- and [100]-zone into the plane of the (001)-pinacoid. If no compensator modulates the intensities of twin domains on (001), the symmetry of twinning leads to equicoloured stripes / (110)-walls (colour plate 1a). By following the traces of the (110)-walls from the (001)- to the (100)- and (010)-faces, we observe a remarkable contrast between (100)- and (010)-domains (colour plate 1c):

The (010) = (a,c)-domains appear very dark for any crystal orientation at crossed polars. Particularly when
reviewed in air these domains seem to be nearly isotropic, where as the (100) = (b.c)-domains are very bright in the diagonal position and show a good extinction in the normal position. The behaviour of the (010)-domains has been interpreted as quasi-isotropic [2], [6]. However, the photometric measurements with crossed polars of the present study (Fig. 7) show anisotropic reflectance on both (100)- and (010)-domains in immersion-oil. The visually observed isotropic behaviour of (010) is the result of a physiological illusion [11], due to the high intensity ratio \( I_{000}/I_{010} \) of light transmitted through the analyzer. The weak intensity of (010)-reflectance follows approximately a \( \cos^3(\psi_s) \)-law (Fig. 7), where \( \psi_s \) represents the angle of the object-stage, and simulates an isotropy next to the strong reflectance of the adjoining (100)-domains.

The Laves-Ernst-compensation as shown in plate 1b, 1d and 1e can be explained as follows:

Plate 1b: if \( Z/P \) and \( \text{sgn}(\sigma) = -1 \) (\( \sigma = -45^\circ \)) ident \( \sigma = +45^\circ \), the domains on (001) show alternatively “blue” addition and “yellow” subtraction colours [7], [9].

Plate 1d: When turning the crystal for 90° around a [100]- or [010]-zone, the (b.c)-domains on (100) show similar “blue” addition, whereas the (a.c)-domains on (010) show a “reddish” subtraction colour.

Plate 1e: if \( Z/P \) and \( \text{sgn}(\sigma) = +1 \) (\( \sigma = +45^\circ \)) ident \( \sigma = +315^\circ \), the compensation colour of the (b.c)-domains changes from “blue” to “yellow”. Comparing the compensation colours of (100)-, (010)- and (001)-domains the change of colour on the (010) = (a,c)-domains is difficult to perceive with the bare eye, but can be proved photometrically. The anisotropy is weak and agrees with the small phase difference of (010) in Figure 12a. When the Laves-Ernst-compensator turns to \( \sigma = +45^\circ \), the colours of compensation on crystal-facets with low phase-difference agree with those of a Lambda-retarder (first-order red) [15].

**Ellipsometric results**

Additional ellipsometric measurements have been made to control the observed and photographically registered differences between ferroelastic domains. Reflected polarized light is characterised by size and orientation of a vibration ellipse relative to the fixed system of the microscope (polarizers and their two bisects 1 and 2). Suitable domains giving reliable ellipsometric results must be selected by aid of the Laves-Ernst-compensator. The appearing colour of compensation verifies where the conditions of optical homogeneity are realised.

As an example, two adjacent (100)- and (010)-domains
Plate 1a to 1f: nearly equidistant widths of stripe domains.

Plate 1a, 1b: domains on (001)-pinacoids.

Plate 1a, 1c: no compensator: the symmetry of crossed polars shows only equiaffining domains on (001) in plate 1a, just as in figure 2e, being separated by the dark reflecting domain walls. Contrary to this result the (100)- and (010)-domains generate intense contrast as shown in plate 1c: on (100) with bright and on (010) with low reflection.

Plate 1b, 1d: idem plate 1a, 1c, but now with Laves-Ernst-compensator inserted, Z°/P Polarizer, sgn(α) = -1 (the λ-plate turns anti-clockwise, α = +45°), the colours of compensation are described as follows: (001)-pinacoid (plate 1b): the (a,b)-domains show "blue addition" if R₁/1 and R₂/2 and "yellow subtraction", if R₂/1 and R₁/1. (100)- and (010)-prism faces (plate 1d): the (b,c)-domains show "blue addition" if R₁/1 and R₂/2 and R₁/1 and the (a,c)-domains show a "reddish subtraction", if R₂/2 and R₂/1. *2 defined at [8] η of the λ-plate.

All photomicrographs shown in the colour plates 1a to 1f and 2a, 2b. Polarized-light microscope (Leitz, ORTHOPLAN-POL): objective 50x/NA. = 0.85 oil-immersion; crossed polarizers θ = 90° = N°; uniaxial reflectivities R₁, R₂ and R₃ in diagonal positions parallel 1 and 2 of the microscope reference system.

Plate 2a and 2b: Single domain area of a (001)-pinacoid (plate 2a) and its opposite side (001)/(plate 2b); the Laves-Ernst-compensator is inserted on both sides. Z°/P sgn(α) = -1 [η] of the λ-plate turns anti-clockwise to α = +30°), both single domain areas shows a "yellow subtraction" color. The comparison of the (001)- and (001)-pinacoid demonstrates perfect correspondence of the domain walls on both sides of the crystal. The edge and vertices of the single domain form a triangular prism, the uniform "yellow subtraction" color of which proves optical homogeneity. The large single domain area of colour plate 2b also is shown in figure 2a, b in contrast of monochromatic light.

Remark:

colour plate 2a and 2b had to be composed of three photographs. Their different depths of colours (saturation of "yellow subtraction") especially on plate 2b is due to automated development of colour prints.
are measured at monochromatic light (Fig. 8a and 8b). The corresponding vibration ellipses in Figures 9a and 9b explain the different behaviour of compensation and extinction on (100) and (010). The light, which is reflected from (010) practically does not need a compensator to be extinguished, because the ellipticity is very small and the ellipse strongly elongated (Fig. 9a). Contrary to the (010)-, the (100)-domain does not extinguish without compensation of its phase difference (Fig. 9b). The vibration ellipse of the reflected light can be measured following the rules and abbreviations of Berek [19].

If the phase-difference \( \delta_{01} \) (Fig. 12a, as measured with a tilting compensator) and the angle \( \Delta \phi_{2} \) of the rotating analyzer comply with the conditions of null-ellipsometry [12], all further parameters as the azimuth \( \eta \) (Fig. 12b), the ellipticity \( \Theta \) (Fig. 12c), the “characteristic angle \( \tau \)” (Fig. 12d) and the ratio of the uniradial reflectivities \( R_{5}/R_{1} \) (Fig. 10 and 11) are calculated.

The azimuth \( \eta \) is strongly related to the birefringence and ratio \( R_{5}/R_{1} \), and particularly well distinguishable in immersion-oil (Fig. 12b): \( \eta(010) > \eta(100) \), whereby the difference increases from blue to red. \( \eta(100) \) decreases from blue (=10°) to values <5° in the red, i.e. \( R_{5} \) (red) approaches \( R_{1} \) (red) as shown in Figure 4. The resulting vibration ellipse looks very similar to those of transmitted light (Fig. 13): a remarkably strong ellipticity, the half-axis of which tend to lie parallel P respectively A (\( \eta = 0 \)), is different from all experience of ore-microscopy in reflected light as tabulated in [13]. The colours of compensation due to birefringence may be confused with those of transmitted light, if a Lambda-plate (first-order red = 551 nm) is used for phase-shifting [14]. But compared with opaque minerals the extremely large ellipticity of YBCO is primarily caused by the dispersion of absorption.

The characteristic angle \( \tau \) (Fig. 12d) proves to be a sensitive test for orthorhombic symmetry. If the three differently oriented principal planes of an anisotropic crystal show obviously different values of \( \tau \), then an uniaxial symmetry of the representation ovaloid of the reflected light can be excluded.

The phase shift between (100)- and (010)-domains can be directly seen, if a tilting compensator is inserted which causes a continuous phase shift within the object field. In white light a “keyboard” of coloured domains (colour plate 1f) and in monochromatic light nearly equidistant stripes of alternating bright and dark (extinguished (100)- and (010)-domains are visible (Fig. 14a).

The domain pattern in monochromatic light can be explained by Figure 14b, those in white light (colour plate 11) schematically in Figure 15: if the 551 nm-isochromatic curve (“first-order red”) of the tilting compensator passes below field diagonal I (area II), then the (010)-domain with its very low phase difference nearly shows the same colour of compensation. Following the ascending path difference of the tilting compensator from area II to area I the colour of compensation changes from “first-order red” to “blue” addition similar to Michel-Levy’s colour table for transmitted light. Contrary to this the adjoining (100)-domain reduces the phase shift of the tilting compensator by its negative phase difference of about-70 nm. Hence the domain colour in area I changes from “blue” = 620 nm to “first-order red” and in area II from “first-order red” to “orange” = 480 nm. The colour of area II following the 551 nm-isochromatic curve of the tilting compensator is similar to that of the Laves-Ernst-compensator in colour plate of oil-immersion, whose actual path difference equals 562 nm (manufactured by Halle in Berlin, Germany).

Using monochromatic light (Fig. 14b), all domains with “first-order red” are extinguished. As a consequence of the different phase shifts in (100)- and (010)-domains extinction occurs alternately in area I for (100)- and in area II for (010)-domains.
Fig. 9a: Figure 9a corresponds with Fig. 8a. The elongated vibration ellipse (= low ellipticity) of (a,c) = (010) enables practically extinction on turning the analyzer alone without retardation by a compensator. Figure 9b corresponds with Fig. 8b: In contrast to (010) the vibration ellipse of (b,c) = (100) enables no extinction without compensation of the phase difference $\phi_{\perp} = 35^\circ$.

Fig. 10 to 12: Ellipsometric parameters calculated from the measured path difference $\Gamma$ and analyzer angle $\Delta \phi_\perp$ for conditions of null-ellipsometry [12].

Fig. 10: Comparison of the ratio $R_\perp/R_\parallel$ for measurements in air (curve 2) and oil (curve 1) on (001), computed from $\Gamma$ and $\Delta \phi_\perp$ as in figure 10.

Fig. 11: Calculated ratio of unidirectional reflectivities $R_\parallel/R_\perp$ versus wavelength.

Fig. 12a to 12d: Phase difference $\delta_{\perp\parallel}$ (a), azimuth $\eta$ (b), ellipticity $\Theta$ (c), and characteristic angle $\psi$ (d), measured in air on (001): $R_\parallel/R_\perp$, $R_\perp/R_\parallel$; on (100): $R_\parallel/R_\perp$, $R_\perp/R_\parallel$; on (010): $R_\parallel/R_\perp$, $R_\perp/R_\parallel$. In Figs. 12a and 12c some curves are dotted for better readability.
Conclusions

Superconducting crystals of YBCO are usually composed of polycrystalline lamella twin domains. The polarized-light microscope enables in situ studies of the domain wall dynamics in order to visualise the ferroelastic wall movements [24]. Mechanical detwining performed under visual control of polarizing microscopy reveals a suitable method for transforming polydomains into single domain crystals [5] [16] [18]. Single domains following the real symmetry of the orthorhombic lattice structure are found out from polydomain material by means of the Laves-Ernst-compensator. They are characterised by homogeneous colours of compensation and can be isolated from polydomains for further investigations. The phenomenon of “puzzle-domains” as described elsewhere [9] [25] can easily be distinguished from the true orthorhombic ferroelastic domains by different compensation methods. In any case an oil-immersed coupling between sample and objective lens enhances the image contrast. It diminishes the influence of light scattering flux residuals on the crystal surface where the increasing refractive index of the coupling medium \(n_0\) enhances the saturation of compensation colours. This can be explained by the phase term \(K = \arctan (2n_0k/n^2+k^2+n_0)\), which changes its value by an increasing \(n_0\) in such a way that the resulting colour coordinates are shifted to higher values of colour saturation [21]. Measurements of anisotropic properties must ensure that there exists no kind of mimetic twinning, the external symmetry of which is higher than that of a single domain or twin component [23]. Otherwise the result of an optical investigation may be inconsistent with the structural status of the crystal. For example, a high density of \{110\}-walls masks the real triaxial symmetry (compare colour plate 2a,b: there exist some areas showing the “first-order red”, where the \{110\}-walls remain under the limit of optical resolution). The polarized-light microscope and its different modes of application like micro-ellipsometry or Differential Interference Contrast of Nomarski [17] gives us a quick answer concerning these problems of the real crystal symmetry.
Polarizing Microscopy

Abstract

The uniradiar reflectivities \( R_i \), \( i = a, b, c \), of an orthorhombic single domain of \( \text{YBa}_2\text{Cu}_3\text{O}_{7.5} \) (YBCO) and their properties in polarized light are reviewed. Whereas the \( (001) \)-pinacoids of YBCO single crystals are thought to be best known, there seems less investigated about the optical character of \( (hk0) \)-prisms. It is evident, that definite results on \( (hk0) \)-prisms are only available, if an oil-immersed optical between crystal and objective is used.

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Bibliography