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Kinetics of α-PcCu → *β*-PcCu Isothermal Conversion in Air and Thermal Behavior of *β*-PcCu from *in Situ* Real-Time Laboratory Parallel-Beam X-ray Powder Diffraction

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The kinetics of the α-PcCu → *β*-PcCu conversion in air has been followed, under isothermal conditions, *in situ* real-time in the 423−443 K temperature range. Data have been fitted following the JMAK model. The reaction order of the kinetics at 423 K is consistent with a diffusion controlled, deceleratory nucleation rate process for 2D laminar particles, whereas at higher temperatures it is consistent with a phase boundary controlled, deceleratory nucleation rate process for 2D laminar particles. At 423 K, the overall transformation mechanism implies three steps: growth of the α-PcCu phase, disordering of adjacent columns of molecules of phthalocyanine, and nucleation and growth of the *β*-PcCu phase. The calculated empirical activation energy is of 187 kJ/mol significantly greater than that for the α-PcCo → *β*-PcCo conversion. This fact seems to support the reported different structures of α-PcCo and α-PcCu. Investigation of the thermal behavior of *β*-PcCu indicates a strongly anisotropic thermal expansion that follows the $\alpha_c \gg \alpha_a \approx \alpha_b$ trend. Moreover, the β angle decreases with increasing temperature. Such anisotropy is consistent with the geometry of the very weak N3···H3 hydrogen bond which acts mainly along the *c* axis.

Introduction

Various polymorphs of copper phtalocyanine (PcCu) have been reported so far.[1] Among them, the α[2] and *β*[3] forms have a known crystal structure. The α-PcCu → *β*-PcCu conversion has been investigated in the past, primarily in organic suspensions, because it is of greatest importance with respect to the decrease of tinting strength and the change of tone in the paint and ink industry.[4,5] Moreover, it is well-known that α-PcCu can be transformed by thermal treatment to the stable *β* polymorph. However, no detailed description of the kinetics of the thermally induced α-PcCu → *β*-PcCu conversion in air is available in reference data, differently from the α-PcCo → *β*-PcCo conversion that was previously reported by our research group from combined energy dispersive X-ray diffraction (EDXD) and differential scanning calorimetry (DSC) data.[6]

According to reference data, α-PcCo and α-PcCu are characterized by distinct crystal structures due to the different molecular packing arising from a different stacking referring to the molecular offset direction.[2] In fact, α-PcCo is characterized by an α(×) stacking, whereas α-PcCu, by an α(+) stacking. This classification arises from the fact that the stacking direction of α-PcCu projected on a molecular plane differs of 45° with respect to that of α-PcPt[7] or α-PcH_2.[8] Nevertheless, it has been suggested[2] that the structure of α-PcCo, determined from X-ray powder diffraction data,[6] was possibly incorrect due to the relatively small differences of the reliability indices for both α(×) and α(+) stacking models obtained for α-PcCu, indicating the possibility that, starting from the α(+) stacking model, smaller reliability indices might have been obtained and suggesting further investigation on the crystal structure of α-PcCo.

However, in the presence of different stacking types, it is possible to hypothesize that such structural differences could lead to different mechanisms of transformation or, at least, significantly different empirical activation energies E_a for the α → *β* conversion.

Therefore, taking advantage of the recent improvements in fast data acquisition detectors, this work aims to investigate, under isothermal conditions, *in situ* real-time the kinetics of the α-PcCu → *β*-PcCu conversion and the thermal behavior of *β*-PcCu in air from laboratory parallel-beam X-ray powder diffraction data.

Experimental Section

Powder of *β*-PcCu (Aldrich product 546682) was used as the starting material for the present work. The α polymorph was obtained by dissolving *β*-PcCu in concentrated H_2SO_4 (96%) followed by reprecipitation by pouring the solution into iced water. The separated solid was washed abundantly with water and dried under a vacuum.

The powder was gently loaded in a 0.7 mm diameter borosilicate glass. X-ray powder diffraction data were collected on a parallel-beam Bruker AXS D8 Advance instrument, operating in transmission in $\theta-\theta$ geometry. The instrument is fitted with a PSD VÅNTEC-1 detector set to a 6° 2θ aperture and a prototype of a capillary heating chamber.[9−11] Data were collected in step-scan mode in the 5−60° 2θ angular range using Cu Kα radiation. A step size of 0.022° 2θ and a counting time of 1 s was used. The kinetics of the polymorphic α → *β* phase transition was studied under isothermal conditions at four different temperatures: 423, 428, 438, and 443 K.

Data were evaluated by the Rietveld method using the Topas software[12] that implements the fundamental parameters approach

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(FPA).[13] This software was selected for its superior performances in peak-shape modeling. Quantitative analysis was carried out using the structural data reported by Hoshino and co-workers[2] for α-PcCu and those obtained in the present work for β-PcCu at the corresponding temperatures. The cell parameters of the two phases and instrumental parameters were also kept fixed to the corresponding average values calculated from all refinements at each temperature before (α-PcCu) and after (β-PcCu) the conversion. Peak position was corrected for sample displacement from the focusing circle. The background was fitted with a 30-term Chebyshev polynomial of the first kind. An absorption parameter (including aluminum contribution from the heating chamber windows) was refined at 303 K and subsequently kept fixed for the remaining patterns. Fractional coordinates for α-PcCu and β-PcCu were unrefined. A global displacement parameter was refined and found to regularly increase with temperature.

After completion of the conversion at 423 K, the capillary was cooled back to room temperature and used to determine the dependence of the structure on temperature of the β-PcCu polymorph. The sample was heated from 303 to 773 K with a step of 10 K. Data were collected in the angular range 5−50° 2θ with a step size of 0.022° 2θ and a counting time of 2.5 s.

Data were analyzed using the GSAS crystallographic suite of programs[14] with the EXPGUI graphical interface.[15] This software was chosen to exploit its extended capabilities to handle constraints on bond distances and angles. Peak shapes were modeled by a pseudo-Voigt function[16] modified to incorporate asymmetry.[17] The peak cutoff was set to 0.2% of the peak maximum. The background was fitted with a Chebyshev polynomial of the first kind. Starting structural parameters were those of ref 3 after conversion to the conventional $P2_1/c$ space group instead of $P2_1/a$ (conversion simply implies switching of a and c), and relabeling of the atoms to the conventional notation for β-phthalocyanes.[18] Complete structure refinements were carried out with intramolecular bond distances and angles (defined as pseudobonds) constrained to the values reported at room temperature (RT).[3] A total of 136 constraints were imposed with a statistical weight of $F = 20$. Moreover, displacement parameters for similar atoms were constrained to be equal. In particular, (a) carbon and nitrogen atoms in the central 16-membered ring and in the isoindole ring were constrained to the same value and (b) displacement parameters for the remaining four carbon atoms of the peripheral benzene ring were constrained to be equal. Hydrogen atom coordinates were refined, whereas displacement parameters were kept fixed to 0.2 Å^2. The absence of preferred orientation was checked and confirmed from evaluation of the corresponding texture indices J determined by means of a generalized spherical-harmonic approach.[19] Therefore, no correction for preferred orientation was applied.

Full structural data are deposited under the form of CIF files as Supporting Information. Full data sets for the kinetics at 423 and 428 K are reported as 3D plots in Figure 1. Examples of Rietveld plots of a single frame of the kinetics at 443 K and of the β-PcCu heating cycle measurement at 703 K are shown in Figure S1 of the Supporting Information.

Discussion

Kinetics of α-PcCu → β-PcCu Conversion. Analysis of the transformed fraction $y(t)$ *vs* time plots shows that the trend of conversion is sigmoidal (Figure 2). Data analysis was performed following the Johnson−Mehl−Avrami (JMAK) model[20−22] on transformed fraction *vs* time plots. This model implies nucleation and growth steps. Data were fitted with the Avrami equation under the general form $y(t) = 1 - \exp^{(-kt)^n}$, where $y(t)$ is the transformed fraction, k is the rate constant, and n is the parameter describing the dimensionality of the reaction mechanism. This expression is found to hold over the greater part (~0.05 < α < 0.9) of a solid state transformation. The exponent n, defined as $n = \beta + \lambda$, where β is the number of steps involved in nuclei formation and λ is the number of dimension in which nuclei grow, is related to the mechanism of reaction. Since n is a compound term, the value determined does not provide a unique value of both β and λ.[23] Therefore, using exclusively X-ray

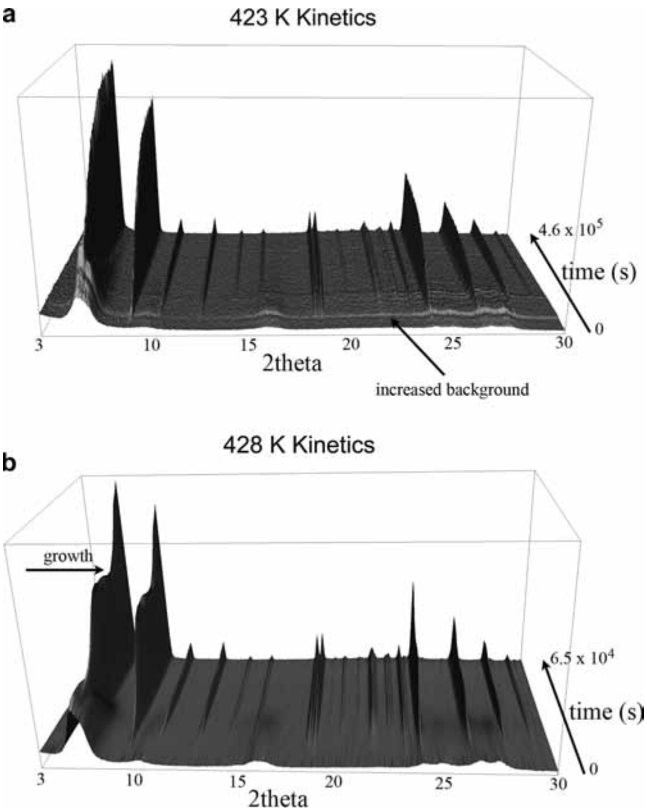

Figure 1. Magnified view (3−30° 2θ) of the full data set used to investigate the isothermal kinetics of the α → β phase transition at (a) 423 K and (b) 428 K. Data are shown as a 3D plot. Arrows indicate the presence of (a) discontinuity of background arising from disordering of adjacent phthalocyanine molecule columns of α-PcCu; (b) intensity increase coupled with sharpening of reflections of β-PcCu due to crystal growth.

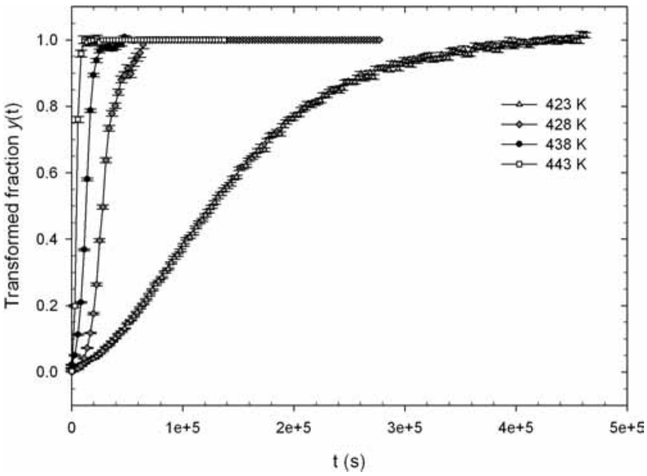

Figure 2. Transformed fraction $y(t)$ *vs* time curves of the isothermal α → β phase conversion at 423, 428, 438, and 443 K.

diffraction techniques is impossible to define completely the mechanism of the polymorphic α → β phase transition from evaluation of the *n* parameter.

TABLE 1: Reaction Order *n*, Rate Constants *k*, and Corresponding Correlation Values R^2 Obtained by Fitting of Transformed Fraction *y*(t) *vs* Time Data with the Avrami Equation

	R^2	*n*	*k*
423 K	0.9995	1.591(6)	$6.29(1) \times 10^{-6}$
428 K	0.9954	2.69(7)	$3.07(2) \times 10^{-5}$
438 K	0.9976	2.57(7)	$6.84(1) \times 10^{-5}$
443 K	0.9995	2.65(4)	$2.010(7) \times 10^{-4}$

The nonlinear fitting process (Table 1) led to very satisfactory correlation values R^2 but clearly indicates an abrupt change of the *n* value passing from 423 ($n = 1.59$) to higher temperatures (*n ca.* 2.65). It is worth noting that the average *n* value of 2.65 is in good agreement with $n = 2.5$ determined for the α-PcCo → β-PcCo conversion from DSC data.[6] Similarly, in that case, only the lowest temperature kinetics was characterized by a significantly different reaction order *n* value of 2. This change can be related to the occurrence of two different mechanisms of reaction. In fact, the average *n* value of 2.65 is consistent with a phase boundary

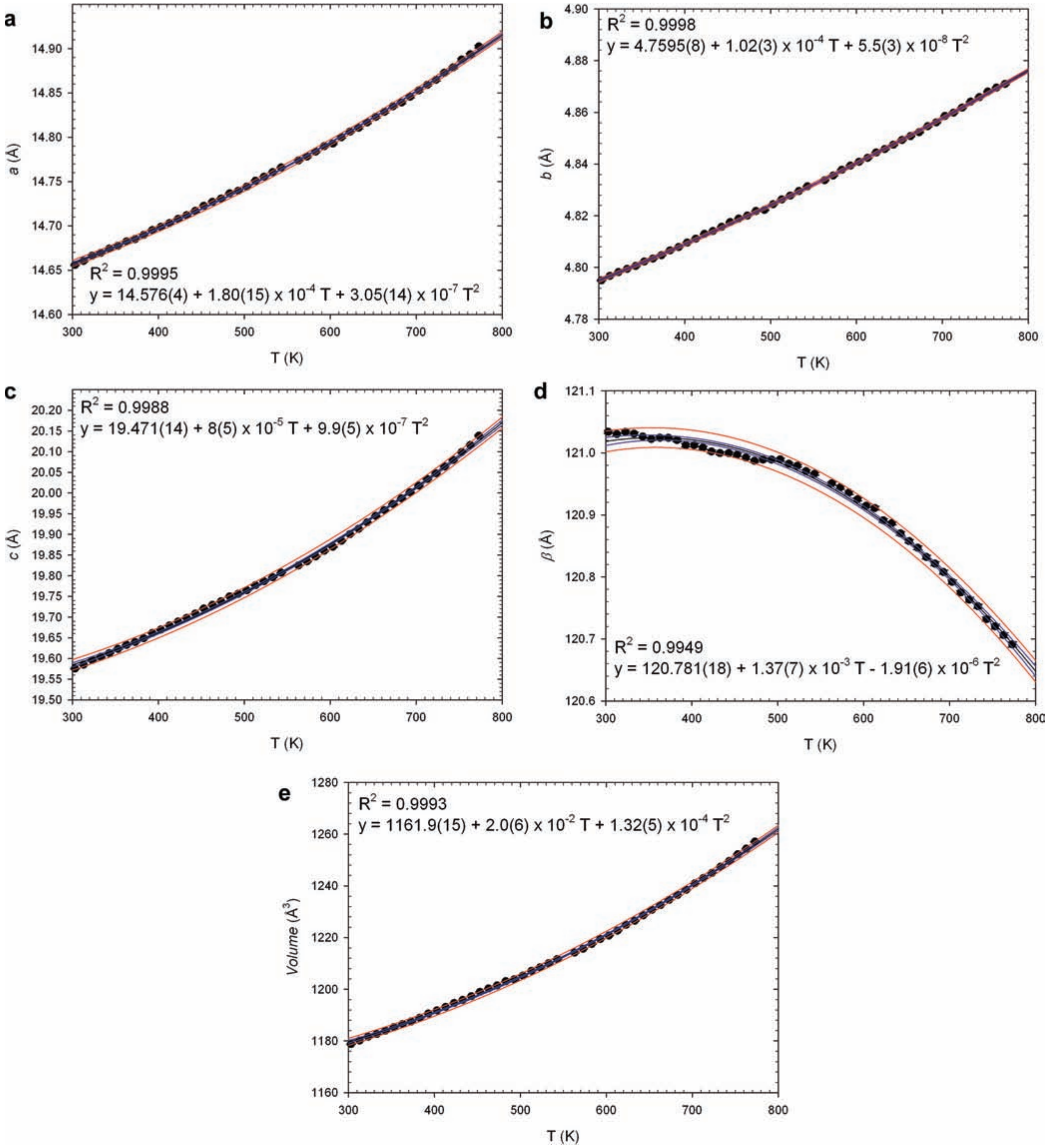

Figure 3. Evolution of lattice parameters and volume of β-PcCu within the 303−773 K temperature range: (a) *a* cell parameter; (b) *b* cell parameter; (c) *c* cell parameter; (d) β angle; (e) cell volume.

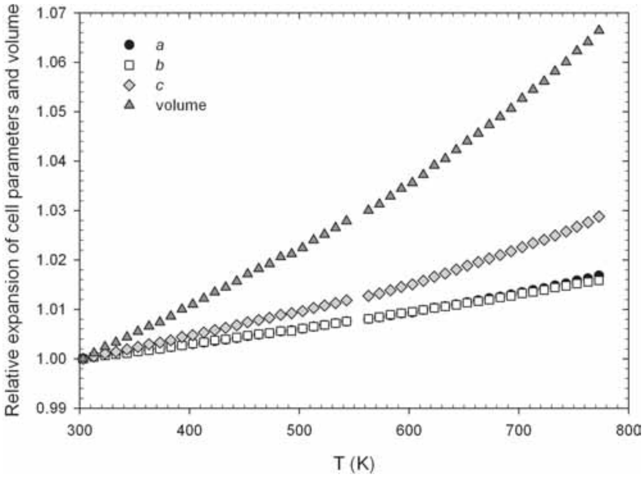

Figure 4. Relative expansion of unit cell parameters and volume for β-PcCu within the 303−773 K temperature range.

controlled, deceleratory nucleation rate process for 2D laminar particles.[24] On the contrary, the n value of 1.59 for the kinetics at 423 K is consistent with a diffusion controlled, deceleratory nucleation rate process for 2D laminar particles.[24]

A close inspection of the raw data of the kinetics at 423 and 428 K indicates relevant differences. First of all, the starting of the conversion at 423 K is preceded by an increase of the intensity of the α-PcCu reflections. Such intensity modification has been observed up to 438 K. On the contrary, the reaction at 443 K is too fast and such a phenomenon was undetected. This behavior has been previously reported for conversions carried out in organic solvents.[4,5] According to the present data, the possible explanation of a preliminary growth without structural modification raised by Kawashima and co-workers[5] seems confirmed.

Moreover, starting of α-PcCu → β-PcCu conversion is preceded by a marked discontinuity indicated by the increase of the background (Figure 1a). This can be due to the production of some low coherence material arising from disordering of adjacent columns of molecules of phthalocyanine from their original α-type arrangement as previously reported for α-PcCo → β-PcCo conversion.[6] On the contrary, a different behavior for kinetics at temperatures exceeding 423 K is observed. In particular, a direct α → β PcCu phase transition is found without the presence of the short-range ordered transient phase hypothesized in the case of 423 K kinetics. This is indicated by the absence of the discontinuity due to the increase of the background. Alternatively, we may consider the presence of this transient phase as a short-lived event that cannot be observed at the time scale of these experiments.

Moreover, at 428 K, it is possible to identify a further growing step indicated by the increased intensity of the reflections of β-PcCu obtained at expenses of a sharpening of the corresponding peaks (Figure 1b). However, the lack of such a growing step at 423 K may be simply due to an insufficient time of analysis (*ca.* 1 week), as, at this temperature, this process could possibly develop very slowly.

Rate constants k and corresponding R^2 correlation values at each temperature are reported in Table 1. Finally, rate constants k for each model were plotted against temperature as $\ln k$ *vs* $1/T$, *i.e.*, the logarithmic form of the Arrhenius equation $k = A \exp^{-(E_a/RT)}$, to calculate E_a (Figure S2 of the Supporting Information) that was found to be of 241 kJ/mol considering data from the four investigated temperatures. However, if data at 423 K are not considered, as they are related to a different mechanism, the calculated empirical activation energy is 187 kJ/mol. The latter value is significantly greater than both activation energies reported in reference data for α-PcCo → β-PcCo conversion for the two distinct transformation mechanisms.[6] On the contrary, the α → β-PcCu conversion occurs at temperatures significantly smaller than those of the α → β-PcCo conversion. Such differences seem to support the occurrence of different molecular packing for α-PcCo and α-PcCu. In fact, α-PcCo is characterized by an α(×) stacking,[2] whereas α-PcCu, by an α(+) stacking referring to the molecular offset direction.[6]

Thermal Behavior of β-PcCu. Structure refinement at RT provided bond distances and angles within 3σ from reference data.[3] The atomic numbering scheme and intramolecular bond distances at RT are reported in Figure S3 of the Supporting Information.

Rietveld refinements of the data collected in the 303−773 K temperature range indicated very regular structural modifications. Data collected at 553 K were not considered because of a sudden shutdown of the heating system during the measurement.

Variation of β-PcCu lattice parameters and volume with temperature are reported in Figure 3 and the corresponding relative expansion in Figure 4. The dependence of lattice parameters with temperature has been empirically modeled with a second-order polynomial of type $p = a_0 + a_1T + a_2T^2$, where a_0 is the value of the corresponding parameter at 0 K, a_1 is the first-order coefficient of expansion, a_2 is the second-order coefficient, and T is the temperature in K.[25] Results of nonlinear fitting are reported in Table 2. The trend of the present data indicates that the expansion of β-PcCu is strongly anisotropic following the $\alpha_c \gg \alpha_a \approx \alpha_b$ trend (in the $P2_1/c$ space group). The β angle decreases with increasing temperature. Rietveld refinements indicate very marginal displacement of the fractional coordinates of non-hydrogen atoms with increasing temperature. As expected, displacement parameters increase as a function of T (Figure S4 of the Supporting Information) with those proper of the carbon atoms of the peripheral benzene ring increasing at a faster rate than the others. Indirect analysis of the N3···H3 hydrogen bond distance evolution as a function of T, deduced from the N3−C5 intermolecular distance, indicates a linear increase from *ca.* 3.34 Å at 303 K to *ca.* 3.64 Å at 773 K (Figure S5 of the Supporting Information). Moreover, dependence on T of the perpendicular distance between successive planes of phthalocyanine molecules along b was also evaluated (Figure S6 of the Supporting Information). Such a distance smoothly increases from *ca.* 3.36 Å at 303 K to 3.49 Å at 773 K, with a bond thermal expansion

TABLE 2: Results from Data-Fitting Procedures Using the Polynomial $p = a_0 + a_1T + a_2T^2$

	a	*b*	*c*	β	*V*
R^2	0.9995	0.9998	0.9986	0.9949	0.9993
a_0	14.576(4)	4.7595(8)	19.471(14)	120.781(18)	1161.9(15)
a_1	$1.80(15) \times 10^{-4}$	$1.02(3) \times 10^{-4}$	$8(5) \times 10^{-5}$	$1.37(7) \times 10^{-3}$	$2.0(6) \times 10^{-2}$
a_2	$3.05(14) \times 10^{-7}$	$5.5(3) \times 10^{-8}$	$9.9(5) \times 10^{-7}$	$-1.92(6) \times 10^{-6}$	$1.32(5) \times 10^{-4}$

approximately half of that of the hydrogen bond. Therefore, the strong thermal expansion of *c* is consistent with the geometry of the very weak N3$\cdots$H3 hydrogen bond which acts mainly along this axis. A further evaluated structural parameter was the angle between the normal to the mean plane of the phthalocyanine molecule and the *b* axis. Such an angle has been found to linearly decrease from *ca*. 45.5° at RT to *ca*. 44.4° at 703 K, indicating a minor rotation (Figure S7 of the Supporting Information). On the contrary, the angle between molecules pertaining to adjacent columns has a more complex dependence on temperature. In fact, it decreases from *ca*. 91° at RT to 90° at 573 K and then it increases to 91.5° at 703 K (Figure S8 of the Supporting Information).

Conclusion

The present work investigated under isothermal conditions the kinetics of the α-PcCu $\rightarrow$ β-PcCu conversion in air and the thermal behavior of β-PcCu from laboratory parallel-beam X-ray powder diffraction. The kinetics has been followed *in situ* real time at four temperatures in the 423−443 K temperature range. Data have been fitted following the JMAK model. Two different mechanisms have been observed as a result of two different *n* values of *ca*. 1.6 and 2.6. In fact, the reaction order of the kinetics at 423 K is consistent with a diffusion controlled, deceleratory nucleation rate process for 2D laminar particles, whereas at higher temperatures it is consistent with a phase boundary controlled, deceleratory nucleation rate process for 2D laminar particles.[24] At 423 K, the overall transformation mechanism implies the following three steps: (a) growth of the α-PcCu phase, (b) disordering of adjacent columns of molecules of phthalocyanine from their original α-type arrangement, and (c) nucleation and growth of the β-PcCu phase. With increasing temperature, step b becomes undetectable due to the fast rate of the conversion. At 443 K, both steps a and b were undetected. The calculated empirical activation energy is 187 kJ/mol after eliminating the rate constant *k* obtained at 423 K arising from a different transformation mechanism, as indicated by different phenomenological *n* values. Such a difference seems to support the occurrence of different molecular packing for α-PcCo and α-PcCu. The thermal behavior of β-PcCu has also been investigated. Thermal expansion of β-PcCu is strongly anisotropic following the $\alpha_c \gg \alpha_a \approx \alpha_b$ trend. Moreover, the β angle decreases with increasing temperature. Such anisotropy is consistent with the geometry of the very weak N3$\cdots$H3 hydrogen bond which acts mainly along the *c* axis. In general, the results of the present work indicate that laboratory parallel-beam X-ray powder diffraction is particularly suited for the investigation of kinetics. The instrumental setup consisting of a capillary transmission goniometer coupled with a PSD allows fast measurements under isothermal conditions. This configuration led to a complete removal of parasitic effects on data collection, as the preferred orientation, allowing, besides reliable and precise quantitative analysis, a full structural characterization of the material in the investigated temperature range.

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Supporting Information Available: Magnified view of fitted X-ray diffraction patterns; Arrhenius plot for the $\alpha \rightarrow \beta$ phase conversion; β-PcCu atomic numbering scheme and bond distances; dependence on *T* of displacement parameters, N3−C5 intermolecular bond distance, perpendicular distance between successive planes of phthalocyanine molecules along *b*, angle between the normal to the mean plane of the phthalocyanine molecule and the *b* axis, and angle between molecules pertaining to adjacent columns. This material is available free of charge via the Internet at http://pubs.acs.org.

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