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Volumetric and x-ray investigations of the crystalline and columnar phases of copper (II) soaps under pressure

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Binuclear copper (II) carboxylates, $Cu_2(C_nH_{2n+1}O_2)_4$, crystallize at room temperature in layered systems in which planes of polar cores are separated by a double layer of alkyl chains. These compounds are mesomorphic in nature above ca. 100 °C. Pseudopolymeric chains of regularly stacked binuclear cores are located at the nodes of a two-dimensional hexagonal lattice and are surrounded by disordered aliphatic chains. The transition from the crystal to the columnar mesophase is characterized by a change in the repeat distance of the binuclear cores along the pseudopolymeric axis. In the crystalline phase, these cores are all oriented in the same direction with a repeat distance of 5.2 Å; in the columnar mesophase, the polar cores are perpendicular to the columnar axis and superposed in a fourfold helicoidal fashion, at least on a local scale, with a repeat distance of 4.7 Å. We present here the effect of pressure on these anisotropic systems in a direction parallel to the columnar axis, and in the plane of the two-dimensional lattice. In a first part, we report the pressure-volume-temperature (P-V-T) relationship of these compounds ($n=12$, 18, and 24) in the temperature range from 30 to 200 °C, and in the pressure range from 1 to 2000 bars. Isothermal compressibility and isobaric expansion are determined in the crystalline and mesomorphic phases. In the mesophase, pressure-volume isotherms can be described by the Tait equation, as in most liquids or molten polymers. In a second part, we discuss the x-ray-diffraction experiments performed under pressure. In the mesophase, the area of the two-dimensional lattice decreases with increasing pressure and, at sufficiently high pressure, the columnar mesophase transforms into a crystalline lamellar phase. By combining P-V-T and x-ray results, we deduce an increase of the stacking period of the binuclear cores as a function of increasing pressure.

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I. INTRODUCTION

Over the past few years, the thermotropic liquid-crystalline polymorphism of transition-metal soaps has been investigated with the experimental techniques usually employed in the field, that is, differential scanning calorimetry, polarizing optical microscopy, x-ray diffraction, etc. [1]. A central theme in this research was the investigation of the structures of linear copper (II) soaps, $[CH_3\,(CH_2)_{n-2}CO_2]_4Cu_2$ (abbreviated in the following to C_nCu), the chemical architecture of which is shown in Fig. 1.

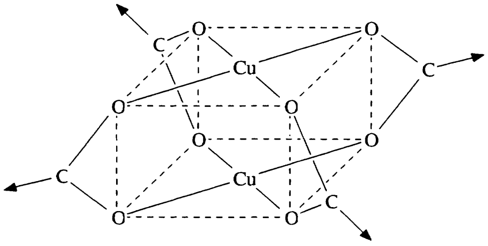

FIG. 1. Schematic representation of the molecular architecture of one copper soap molecule: arrows indicate the departure of the four aliphatic chains from the central copper-oxygen core.

In the condensed state, the molecules of copper soaps are connected to one another (pseudopolymerized) by axial ligation of the copper and oxygen atoms, as shown in Fig. 2. In the crystalline state at low temperature, the axial intermolecular ligation involves homologous oxygen atoms [O(1),O(1′),. . .] and leads to the formation of columns of "tilted" polar cores [Fig. 3(a)] with a stacking period [2] of about 5.2 Å. Parallel to one another, the columns are set side by side into plane layers, themselves separated by a double layer of conformationally extended alkyl chains [2,3].

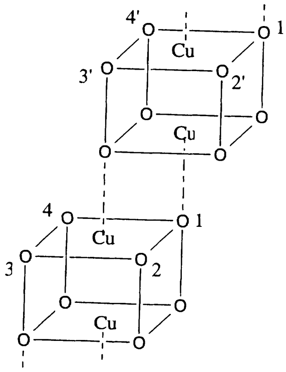

FIG. 2. Schematic representation of the axial coordination (dashed lines) of the copper atoms of two neighboring molecules.

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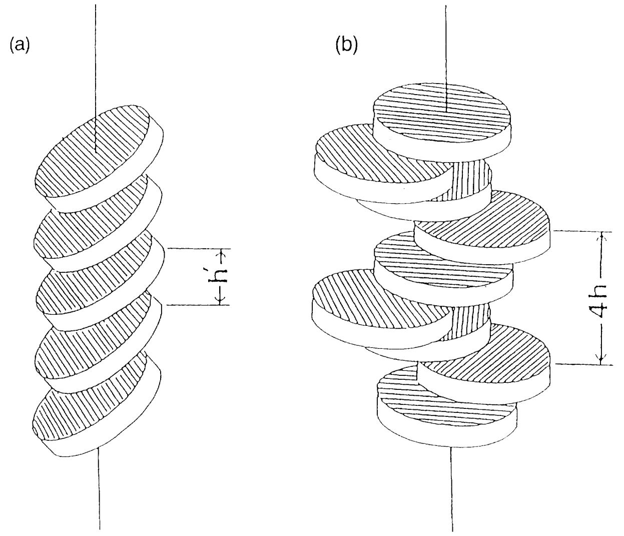

FIG. 3. Schematic representation of the stacking of the soap polar heads in (a) the crystalline and in (b) the columnar mesomorphic state.

When heated above ca. 120 °C, the copper soaps display columnar liquid-crystalline phases, hexagonal in symmetry. The tetragonal polar cores of the molecules are still connected to one another by axial ligation of the copper and oxygen atoms, but the columns obtained now are characterized by a stacking period [4,5] of only 4.65 Å. Compared to that deduced from the known bond lengths and atomic sizes, this period suggests that the polar cores are oriented with their fourfold axis of symmetry parallel to the columnar axis. As shown in Fig. 3(b), the piling mode has been tentatively described to be helicoidal, going through circular permutation of the oxygen atoms involved in the axial ligation [O(1),O(2),O(3),O(4),O(1′),...,; see Fig. 2]. With the experimental evidence available, the one-dimensional extension of the helicoidal array of the cores remains unknown and the possible existence of defects corresponding to a sign change of the helix cannot be discarded. Yet the absence of three-dimensional correlations among the columns (as surmised from the x-ray patterns) suggests that the helices are either imperfect or noncrystallographic (as in the case of polypeptides). The columns are separated from one another and surrounded by the paraffin chains spreading outward in a disordered conformation. The stacking period of the polar cores along the columnar axis turn out to be independent of the length of the alkyl chains and of the temperature. Oriented parallel to one another, the columns are assembled following a two-dimensional hexagonal crystal lattice.

One of the important features of the columnar ordering of copper soaps, clearly demonstrated using the extended x-ray absorption fine structure (EXAFS) technique [6] is that, despite the liquidlike state of the paraffin chains, the polar cores are definitely superposed in a compact and well-defined fashion. Taking into account the fundamental anisotropy of these materials, liable to lead to a highly anisotropic compressibility, we thought it of interest to undertake a systematic investigation of the influence of pressure, both in their thermotropic polymorphism and in their structural crystallographic behavior. It is fair to mention at this point that pressure has already been considered in the past as an important thermodynamic variable affecting the thermotropic polymorphism [7] and sometimes even inducing new mesophases [8]. In the particular case of smectic-*A* liquid crystals, pressure was found to leave the interlayer spacing unperturbed, and thus to probably have an effect only on the lateral compressibility of the molecules [9].

In the present paper, we describe a thermodynamical and structural study of three copper (II) soaps, namely, $C_{12}Cu$, $C_{18}Cu$, and $C_{24}Cu$, in a temperature range from 30 to 200 °C, up to a pressure of 2 kbar. Using a *P*-*V*-*T* technique, we first measure the pressure and temperature dependence of the specific volume of these compounds and determine their phase behavior. Then, using x-ray diffraction, we analyze the influence of pressure upon the structural parameters of the columnar mesophase, especially with reference to the intracolumnar stacking period of molecules.

II. EXPERIMENT

A. Volume measurements

P-*V*-*T* measurements in this work were performed using a Gnomix Research apparatus, designed by P. Zoller *et al.* [10]. The sample (about 1–2 g), carefully degassed and molded, was contained in a rigid cell, one end of which is closed by a flexible metal bellows. The space in the cell not taken up by the sample was filled with mercury under vacuum. The pressure was applied with a hand pump, using silicone oil as the pressure-transmitting fluid. The displacement of the bellows, measured by a linear variable differential transformer, was converted to a volume change of the sample making use of the cross-sectional area of the bellows, the known *P*-*V*-*T* properties of mercury, and a correction function determined in a separate experiment with the cell entirely filled with mercury. To measure the specific volume of the sample as a function of temperature and pressure, it is necessary to calibrate the instrument by introducing in the data-treatment software the value of the specific volume at 30° C under a pressure of 1 bar. This value not being available in the literature, the calibration of the instrument was run using a value properly adjusted to yield the known value of the specific volume in the columnar mesophase at 150 °C under a pressure of 1 bar [11].

From a methodological standpoint, two distinct experimental modes of operation were followed: the isothermal and the isobaric. In the first case, the temperature was kept constant with an accuracy of 0.1 °C and the volume measurements were performed in the pressure range from 100 to 2000 bars with steps of 100 bars. Values given for zero pressure were extrapolated automatically by the instrument. In the second case, the pressure was maintained constant by manual adjustment and the volume measurements were performed every 0.8 °C.

B. X-ray-diffraction experiments

X-ray-diffraction experiments in this work were performed using a vacuum small-angle camera equipped with a bent gold-plated glass mirror (nickel-filtered $K\alpha$ copper radiation from a GX-20 Elliott rotating anode x-ray generator) and a CEA-LETI linear position-sensitive detector. Exposure times of 30 minutes allowed registration of the diffraction peaks (more than 5000 counts at the peak maximum) with an accuracy of about 0.3 Å. The instrument was calibrated using the known values of the intercolumnar spacings at ambient pressure [3].

The samples were contained in a specially designed pressure cell manufactured by Nova-Swiss (France), similar to that already described elsewhere [9]. This cell consists of one part containing the pressure-transmitting fluid (silicon oil) and a second part containing a beryllium cylinder (7 mm in diameter) in a cylindrical cavity (2 mm in diameter) in which the sample is enclosed. The two parts are held together tightly by two screwed aluminum castings, and the pressure is transmitted to the sample through a beryllium piston. The pressure, up to 2 kbar, was applied with a hand pump and measured with a Manganin gauge to an accuracy of 0.5 bar. The whole pressure cell was electrically heated and thermally insulated with glass wool. The temperature was controlled within 1 °C up to 200 °C.

III. VOLUMETRIC STUDY

A. General behavior

The isothermal polymorphic behavior with regard to pressure (piezotropism) of the copper soaps considered in this work is shown in Figs. 4–6. It is of interest to note immediately that the values corresponding to $C_{18}Cu$ and $C_{24}Cu$ at room pressure are in quantitative agreement with those determined previously by dilatometry [5]. Close inspection of the data leads to the following comments. As expected, the specific volume decreases appreciably with increasing pressure, this effect being significantly more pronounced for the mesophase, which contains the paraffin chains in the "molten" state, than for the crystal, where the molecules are entirely "crystallized." For a given phase, the pressure dependence of the volume clearly shows the compressibility to increase with temperature as usually found in condensed matter. Finally, the transformation of the mesophase into the crystal, which takes place gradually for kinetic reasons related to

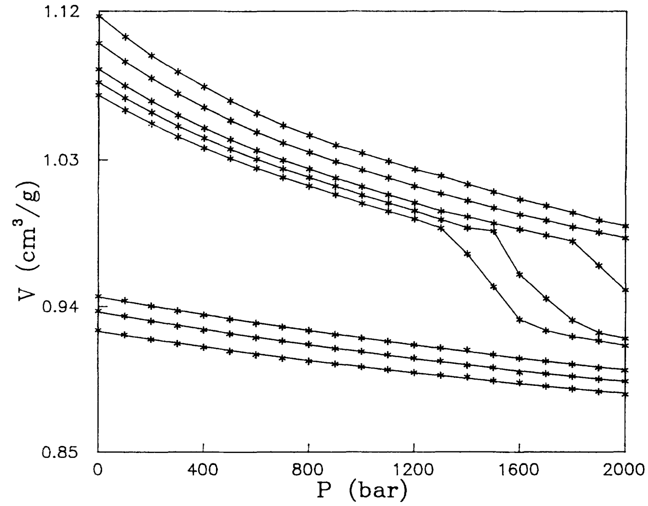

FIG. 5. Isothermal variation of the specific volume of $C_{18}Cu$ as a function of pressure, measured at a series of temperatures for the crystal and the mesophase. Curves from top to bottom correspond successively to the following temperatures: 190, 170, 150, 140, 130, 90, 67, and 30 °C.

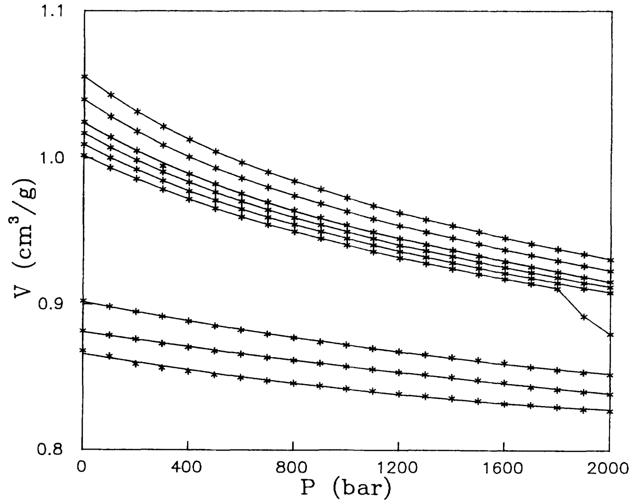

FIG. 4. Isothermal variation of the specific volume of $C_{12}Cu$ as a function of pressure, measured at a series of temperatures for the crystal and the mesophase. Curves from top to bottom correspond successively to the following temperatures: 190, 170, 150, 140, 130, 120, 90, 67, and 30 °C.

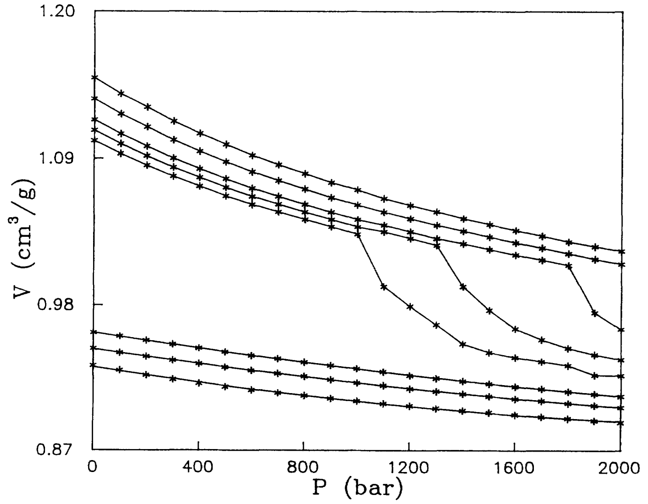

FIG. 6. Isothermal variation of the specific volume of $C_{24}Cu$ as a function of pressure, measured at a series of temperatures for the crystal and the mesophase. Curves from top to bottom correspond successively to the following temperatures: 190, 170, 150, 140, 130, 90, 67, and 30 °C.

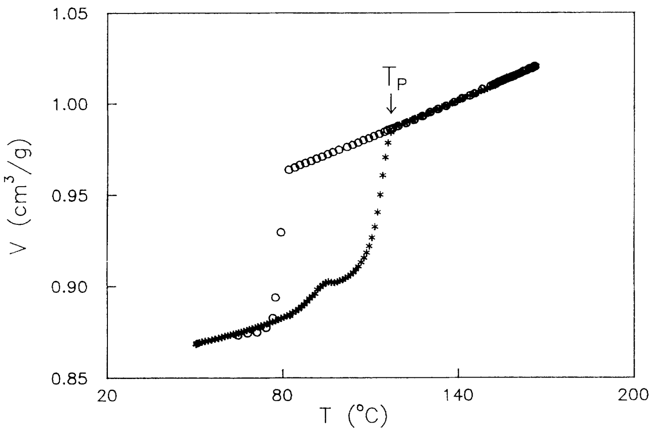

FIG. 7. Isobaric variation of the specific volume of $C_{12}Cu$ as a function of temperature, measured upon heating (asterisks) and cooling (open circles) at a pressure of 100 bars for the crystal and the mesophase. Arrow shows the transition from the crystal into the mesophase upon heating.

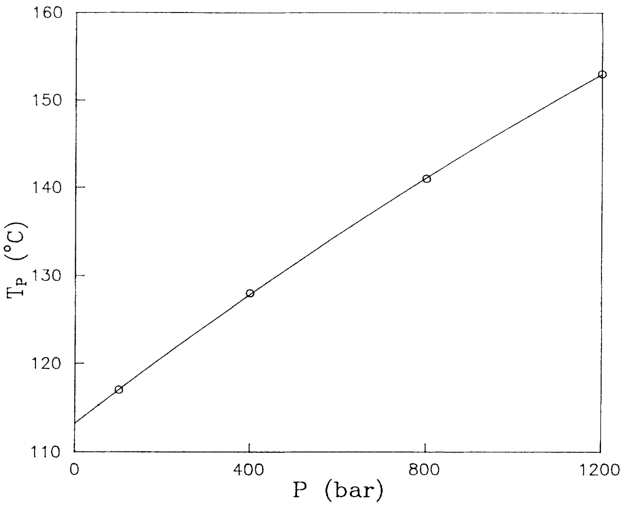

FIG. 9. Pressure dependence of the transition temperature (defined as shown in Figs. 7 and 8) from the crystal into the mesophase for $C_{12}Cu$.

the nucleation process, is accompanied by an important decrease of the volume.

The isobaric polymorphic behavior of copper soaps with respect to temperature (thermotropism) is illustrated in Figs. 7 and 8 for $C_{12}Cu$ and $C_{24}Cu$. The transition upon cooling from the mesophase into the crystal takes place with a strong hysteresis (of about 30 °C) related to the nucleation of the crystallization process. Values obtained at a given temperature are perfectly reproducible in the high-temperature mesomorphic state, regardless of whether the temperature was reached by cooling or heating. Even though suggesting kinetic effects, the volume variation at the transition between the crystal and the mesophase is much more abrupt here than it is in isothermal conditions, thus making it possible to determine the transition temperature at constant pressure with reasonable accuracy. Figure 9 illustrates the pressure dependence of this temperature in the particular case of $C_{12}Cu$. It is of interest to note, finally, that the isobar of $C_{12}Cu$ registered upon heating reveals the presence of a bump just before the mesophase is obtained; as checked by x-ray diffraction, this corresponds to the appearance of an intermediate crystalline phase, lamellar in nature.

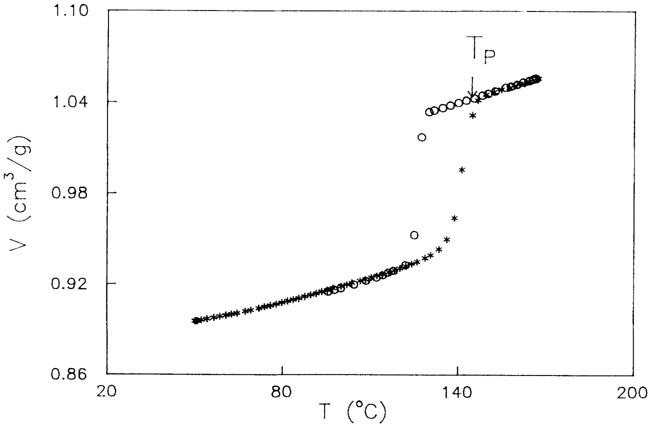

FIG. 8. Isobaric variation of the specific volume of $C_{24}Cu$ as a function of temperature, measured upon heating (asterisks) and cooling (open circles) at a pressure of 500 bars for the crystal and the mesophase. Arrow shows the transition from the crystal into the mesophase upon heating.

B. Crystal behavior

As is well-known, mesogenic substances at low temperature currently show more than one different crystalline polymorphic form, which sometimes coexist for kinetic reasons. In addition, cracks and voids are often produced during the crystallization process from the melt, due to the important volume contraction of the material. This is why a rigorous quantitative analysis of the specific volume in the crystal, particularly comparison of the molar volumes on an absolute scale, is not always meaningful.

Such being the case of copper soaps as already observed by dilatometry at room pressure [5], no sustained attempt was made in the present work to exploit the experimental data in much detail. The measured specific volumes were thus simply expressed in a coherent way as a single function of two variables, $v = f(t,P)$, approximated by the following quadratic form:

$$v(T,P) = a + bT + cP + dT^2 + eP^2 + fTP .$$

The experimental values of v were analyzed by a least-squares method in the temperature range from 30 to 90 °C and in the pressure range from 1 to 2000 bars. The calculated values of the coefficients a to f for each soap are reported in Table I. Curves in Figs. 4–6 illustrate the quality of the fit between the calculated $v(T,P)$ functions and the experimental data.

C. Liquid-crystal behavior

As equilibrium is easily and thoroughly reached in the fluid mesomorphic state, the experimental data collected

TABLE I. Coefficients for the least-squares fits to the experimental isotherms in the crystal (see Figs. 1–3). $v(T,P)=a+bT+cP+dT^2+eP^2+fTP$.

Parameters	$C_{12}Cu$	$C_{18}Cu$	$C_{24}Cu$
a ($cm^3\,g^{-1}$)	0.8568 ± 0.0011	0.9156 ± 0.0008	0.9182 ± 0.0006
b ($10^{-4}cm^3\,g^{-1}\,°C^{-1}$)	0.96 ± 0.38	1.33 ± 0.25	2.85 ± 0.15
c ($10^{-5}cm^3\,g^{-1}\,bar^{-1}$)	-2.38 ± 0.09	-2.35 ± 0.06	-2.67 ± 0.07
d ($10^{-6}cm^3\,g^{-1}\,°C^{-2}$)	4.00 ± 0.31	1.84 ± 0.19	1.68 ± 0.10
e ($10^{-9}cm^3\,g^{-1}\,bar^{-2}$)	3.78 ± 0.34	2.95 ± 0.25	4.98 ± 0.29
f ($10^{-8}cm^3\,g^{-1}\,°C^{-1}\,bar^{-1}$)	-8.28 ± 0.88	-5.57 ± 0.59	-9.32 ± 0.42

may now be analyzed with confidence. They were analyzed coherently by a least-squares method involving a two-variable function $v=g(T,P)$.

It is the general opinion that the P-V-T behavior of most liquids and amorphous polymers may advantageously be described in terms of the so-called Tait equation of state [12,13]:

$$v(T,P)/v(T,0)=1-C\ln[1+P/B(T)]\ ,$$

where C is a dimensionless universal constant equal to 0.0894, and where $B(T)$ is an exponential function of temperature solely, $B(T)=B_0\exp(-B_1T)$, having the dimension of a pressure. It is this very equation that, quite naturally, was also used in the present work.

The experimental values of v were analyzed isothermally and separately for each soap in the temperature range from 130 to 200 °C and in the pressure range from 1 to 2000 bars. By injecting the instrumentally extrapolated value of $v(T,0)$, the individual values of C and $B(T)$ were deduced. It is important to point out that the C values found here were all actually the same ($C=0.0889\pm0.0020$) whatever the temperature and the soap considered, and also very close to the universal value reported in the literature. As for $B(T)$, it decays exponentially with temperature as expected, with B_0 and B_1 values (see Table II) comparable to those given in the literature for various chain molecules (polymers) [13]. The Tait equation holds, therefore, very satisfactorily for the columnar liquid-crystalline phases of copper soaps, as it commonly does for many organic liquids and amorphous polymers (see Figs. 4–6).

Starting from the experimentally determined $v(T,P)$ functions, it is of course very easy to calculate analytically the isobaric thermal expansion coefficient $\alpha=(1/v)(\delta v/\delta T)_P$ and the volume compressibility at constant temperature $\beta=-(1/v)(\delta v/\delta P)_T$ as a function of temperature and pressure within the stability range of the columnar mesophase. The relevant expressions are

$$\beta(T,P)=\{(P+B)[1/C-\ln(1+P/B)]\}^{-1}\ ,$$

$$\alpha(T,P)=\alpha_0-\beta(T,P)PB_1\ .$$

The α expression uses the α_0 values (see Table III) calculated by a least-squares method through the equation

$$v(T,0)=v_0\exp(\alpha_0T)$$

from the $v(T,0)$ values directly provided by the P-V-T instrument. It is of interest to note that $\alpha_0=\alpha(T,P=0)$ represents the thermal expansion coefficient at zero pressure, and its value, of the order of 7×10^{-4} K^{-1}, is in perfect agreement with what is generally found for liquid

TABLE II. Least-squares fit of $B(T)=B_0\exp(-B_1T)$.

Soap	B_0 (bar)	B_1 ($10^{-3}\,°C^{-1}$)
$C_{12}Cu$	1963	5388
$C_{18}Cu$	1912	4912
$C_{24}Cu$	1517	3521

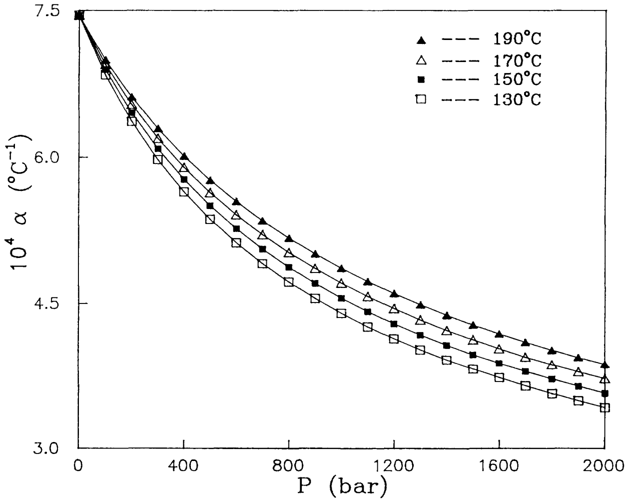

FIG. 10. Pressure dependence of the isobaric thermal expansion coefficient of $C_{12}Cu$ at different temperatures.

TABLE III. Least-squares fit of $v(T,0)=v_0\exp(\alpha_0 T)$.

Soap	v_0 (cm^3/g)	α_0 (10^{-4} °C^{-1})
C_{12}Cu	0.9150	7.45
C_{18}Cu	0.9685	7.27
C_{24}Cu	1.0036	7.02

crystals. As expected for molecular crystals and organic materials [14], $\alpha(T,P)$ decreases as a function of pressure and increases with temperature (Fig. 10); on the other hand, $\beta(T,P)$ decreases as a function of pressure and increases with temperature (Fig. 11).

IV. X-RAY-DIFFRACTION STUDY

A. General behavior

Typical examples of recorded x-ray patterns are given in Fig. 12, showing reflections in the ratio $1:\sqrt{3}$ for the columnar mesophase, and reflections in the ratio 1:2:3 for the lamellar crystalline phase. It is important to note explicitly that the number and sharpness of the reflections remain unchanged whatever the pressure. For the sake of experimental convenience, the pressure dependence of the copper soap structure was studied in isothermal conditions only. Setting the samples in the columnar state at 130 and 150 °C, the pressure was stepwise increased starting from room pressure up to 1200 bars, until the samples fully crystallized; the pressure was then decreased for the system to reenter the columnar state. Figure 13 illustrates the variation of the intercolumnar and/or the interlamellar spacing as a function of pressure in the case of C_{12}Cu. It is clear that the transition upon increasing pressure from the columnar mesophase into the lamellar crystal takes place progressively in the pressure range from 800 to 1000 bars, through a two-phase regime indicative of a nucleation process and of slow kinetics of crystallization as mentioned previously in the volumetric study of the soaps. As usual, the reverse transition occurs abruptly at about 800 bars.

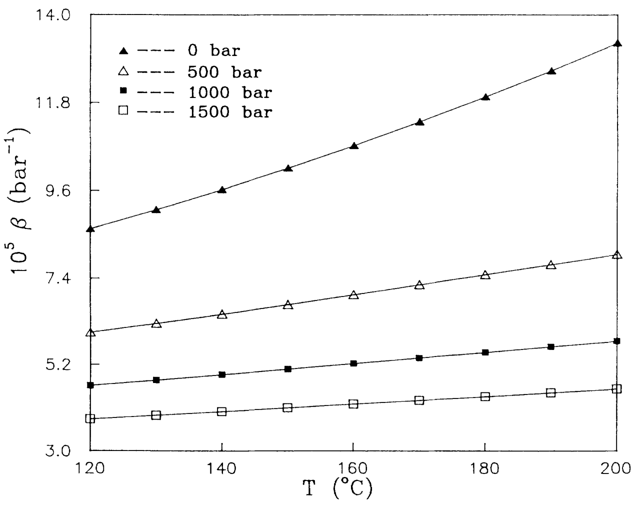

FIG. 11. Temperature dependence of the isothermal volume compressibility of C_{12}Cu under different pressures.

B. Crystal behavior

Simple inspection of Fig. 13 shows the lamellar period in the crystalline state to vary weakly with pressure. A linear least-squares fit of the experimental data in the pressure range from 820 to 1150 bars leads to the equation d (Å)$=31.57+0.00039P$ (bars). This equation suggests the following two comments. First, the spacing at zero pressure is in perfect agreement with that (31.52 Å) found previously for copper soaps at ambient pressure [3]; this means that the lamellar crystal induced by pressure is identical to the crystal observed in usual conditions. Second, the isothermal pressure dependence of the spacing, $(1/d)(\delta d/\delta P)=+1.2\times10^{-5}$ bar^{-1}, is unexpectedly positive; this indicates that the tilt angle of the soap molecules with respect to the lamellar normal decreases with increasing pressure. Such a behavior is easy to understand considering the pressure dependence of the molecular area S, which is negative. Knowing, indeed, that the volume of one soap molecule, V, equals the prod-

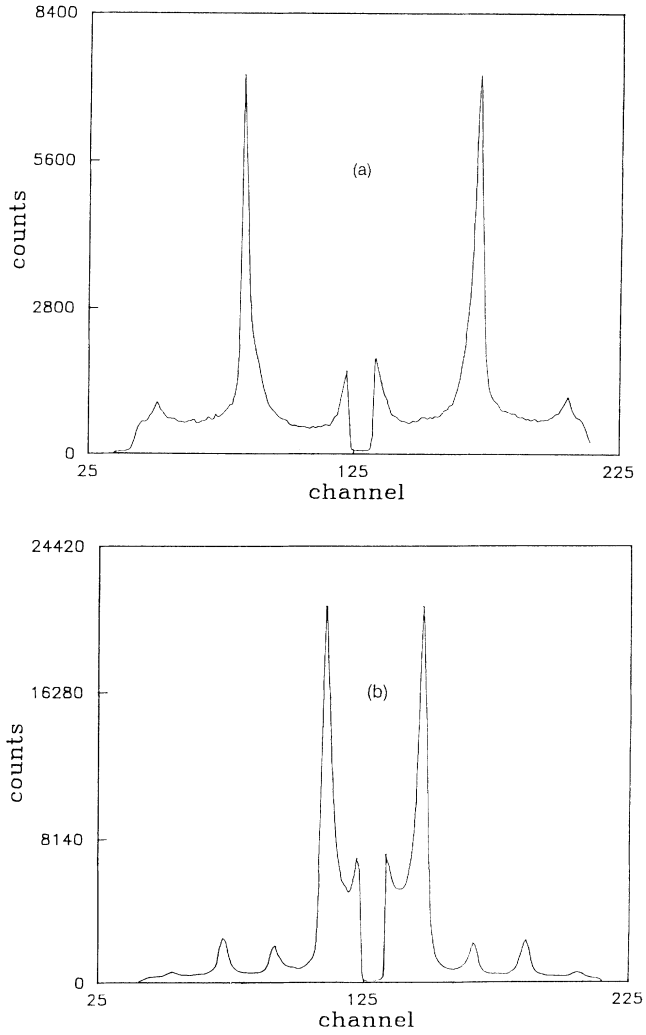

FIG. 12. Typical examples of small-angle x-ray patterns of C_{12}Cu registered at 130 °C under a pressure of (a) 1 bar for the columnar mesophase and (b) 1100 bars for the crystalline phase.

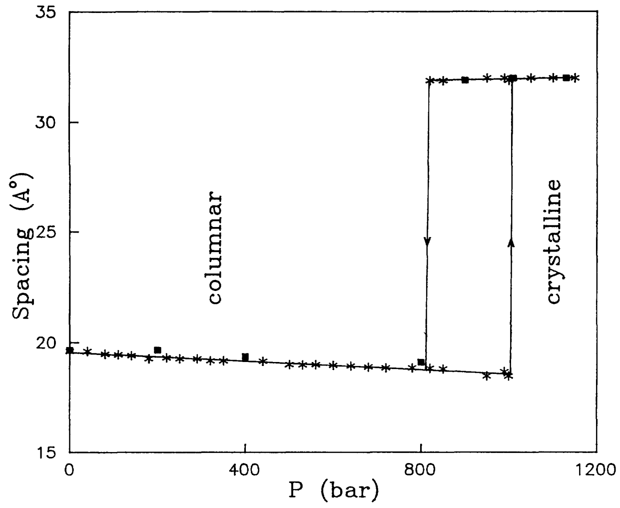

FIG. 13. Variation of the intercolumnar and/or the interlamellar spacing of $C_{12}Cu$ as a function of pressure. Asterisks and solid squares represent measurements at increasing and decreasing pressures, respectively.

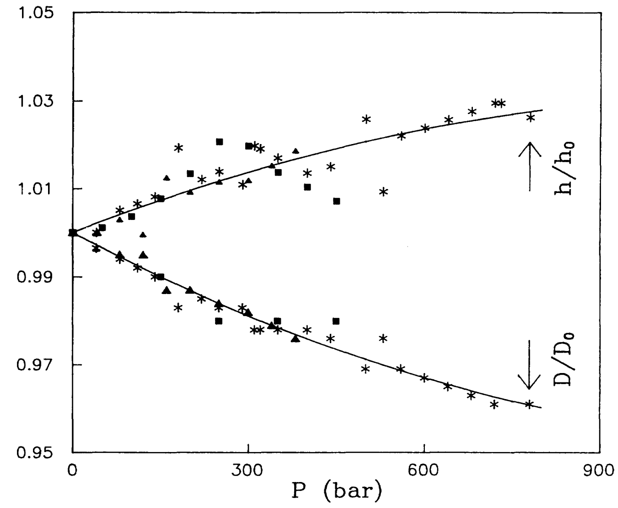

FIG. 14. Pressure dependence of the relative intercolumnar spacing D/D_0 and the relative intracolumnar stacking period h/h_0 of $C_{12}Cu$ (asterisks), $C_{18}Cu$ (squares), and $C_{24}Cu$ (triangles) in the mesomorphic state at 130 °C. D_0 and h_0 correspond to zero pressure. Curves are guides for the eye.

uct Sd, it is clear that;

$$\left(\frac{1}{S}\right)\left(\frac{\delta S}{\delta P}\right)_T = \left(\frac{1}{V}\right)\left(\frac{\delta V}{\delta P}\right)_T - \left(\frac{1}{d}\right)\left(\frac{\delta d}{\delta P}\right)_T$$

$$= -\beta - \left(\frac{1}{d}\right)\left(\frac{\delta d}{\delta P}\right)_T ,$$

and taking for β an approximate value of 3×10^{-5} bar^{-1} ($\beta = c/a$, Table I), one finds $(1/S)(\delta S/\delta P)_T \cong -4\times10^{-5}$ bar^{-1}.

C. Liquid-crystal behavior

Further inspection of Fig. 13 shows the intercolumnar spacing D in the liquid-crystalline state to depend appreciably upon pressure. The extent and direction of the variation of D vs P are better shown in Fig. 14, where the variation of the intracolumnar stacking period h is also represented. This parameter was calculated using the experimental values of $v(T,P)$ given above and the well-known relation [3]

$$(\sqrt{3}/2)D^2h = v_M/\mathcal{N}$$

where v_M is the molar volume of the soap and $\mathcal{N}$ is Avogadro's number. Comparison of the pressure dependences of D and h clearly shows the action of hydrostatic pressure on the columnar mesophases of copper soaps to result in a very significant anisotropic deformation of the structure. The corresponding compressibilities at 130 °C, calculated by a linear least-squares fit method, are

$$-(1/D)(\delta D/\delta P) = 7.1(\pm0.3)\times10^{-5}\ \text{bar}^{-1}$$

and

$$-(1/h)(\delta h/\delta P) = -5.4(\pm0.6)\times10^{-5}\ \text{bar}^{-1} .$$

The very existence of this anisotropy is not surprising at all, as the columnar systems are of uniaxial symmetry. However, the comparative pressure dependences of D and h are remarkable and totally unexpected; contrary to D/D_0, which decreases quite normally, h/h_0 increases appreciably upon compression. The increase of h corresponds to a stretching of the columnar cores. Starting from $h = 4.65$ Å at room pressure, with the polar cores oriented perpendicular to the columnar axis, the stacking period increases to about 4.8 Å at a pressure of 800 bars, thus getting over a good deal of the distance to the period (5.2 Å) characteristic of the crystal. No doubt, the stretching of the columns goes parallel to the tilting of the molecules and thus the action of pressure amounts to bringing the stacking mode of the polar heads nearer to that of the crystal.

Before discussing the pressure expansion of h, it is useful to note that, within the experimental errors (1%), D/D_0 and h/h_0 change exactly in the same way for all of the soaps considered, independently of the molecular weight and temperature. This behavior is in compliance with the idea that, in the amphiphilic copper soaps, the two antagonistic molecular moieties act independently from one another [15]. The polar copper carboxylate heads, which interact strongly with one another, pile up in their own way and the pressure dependence of their stacking period is independent of the length of the aliphatic chains, whereas the aliphatic chains themselves are liquidlike in character and therefore susceptible to occupy uniformly the spaces left empty in between the polar cores.

The stretching of the columns is hard to understand readily because the stacking mode of the polar cores is dominated by the axial ligation of the copper and oxygen atoms. However, closer inspection of the local structure of the columns in the mesomorphic and crystalline phases permits one to get an idea of the mechanism possibly involved. While rather smooth in the crystal [Fig. 3(a)] the outer surface of the columnar polar core is significantly rougher in the mesomorphic phase [Fig. 3(b)], decorated as it is with a number of hollows between the protruding polar cores. The size of the hollows is comparable to that of the methylene—CH_2— groups; the aliphatic chains therefore can hardly go into them and the periphery of the columnar cores is not very compact. The action of pressure, generally tending to increase the compactness of matter, would then result here in reducing the roughness of the columnar surface.

This might be achieved either by pushing the polar heads of the molecules away from one another along the columnar axis, thus keeping their orientation unchanged, or else by modifying the sequence of the oxygen atoms involved in the axial ligation, thus progressively opening up the peripheral hollows by tilting the molecular polar heads with respect to the columnar axis. The first mechanism severely damages the axial ligation and coordination of the molecules and, more importantly, it reduces the compactness even though it reduces the overall roughness. On the contrary, the second mechanism preserves the ligation of the molecules and seems by far more convenient.

The presence of hollows at the surface of the columnar polar cores, and their progressive filling with the molten aliphatic chains as pressure is increased, is attested, at least qualitatively, by the pressure dependence of the intensity of the first Bragg harmonic of the hexagonal columnar packing, shown in Fig. 15. Considering their radial electron-density distribution, the columnar polar cores at zero pressure appear thinner than at high pressure, due to the presence of hollows; the corresponding intensity distribution as a function of reciprocal spacing is then wider (Fig. 16). When pressure is applied, the apparent radius of the cores increases due to the progressive filling of the hollows and the intensity decreases drastically. This effect is more pronounced for shorter soap molecules because the corresponding columnar Bragg reflection occurs at larger reciprocal spacings, as shown by arrows and the inset curve in Fig. 16(b).

The progressive tilting of the molecules, starting from the upright helicoidal arrangement of the molecules at zero pressure and leading to the all-tilted arrangement seen in the crystal (Fig. 13), deserves the following comment. This progressive tilting can take place very simply by introducing defects along the helix (by skipping, for instance, one oxygen atom in the circular permutation).

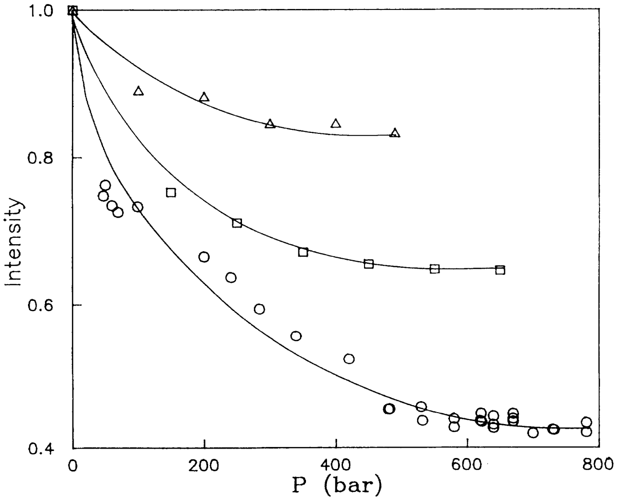

FIG. 15. Pressure dependence at 130 °C of the intensity of the first Bragg harmonic of $C_{12}Cu$ (circles), $C_{18}Cu$ (squares), and $C_{24}Cu$ (triangles) in the hexagonal columnar mesophase. Intensities at zero pressure are taken equal to unity.

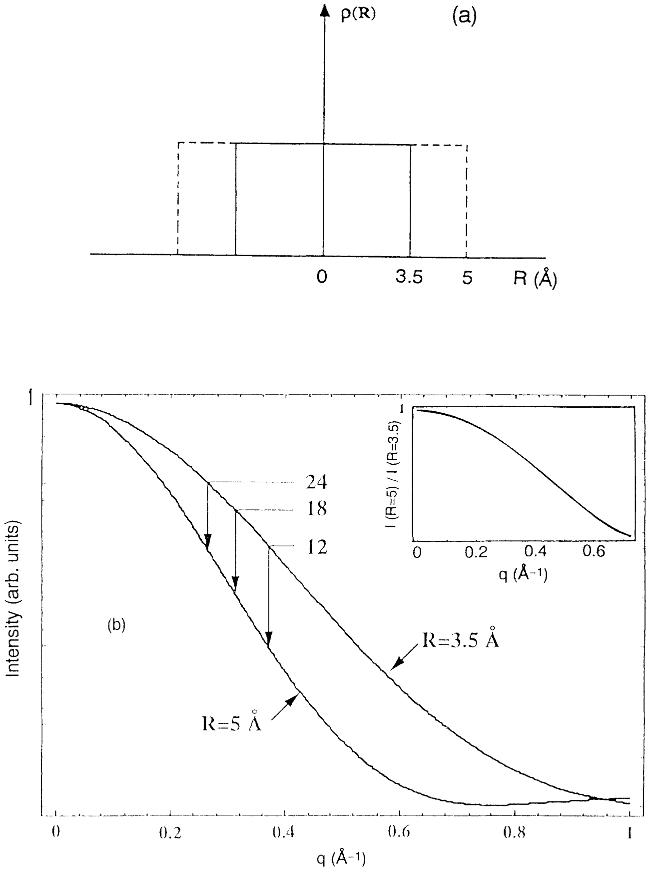

FIG. 16. Schematic representation of (a) the radial electron-density distribution of the columnar core and (b) the corresponding intensity distribution calculated as $[J_1(qR)/qR]^2$, where J_1 is the first-order Bessel function. Intensities at $q=0$ are taken equal to unity. Arrows indicate intensity variations with R at three reciprocal spacings corresponding to the first-order Bragg reflection of the $n=12$, 18, and 24 copper soaps. Inset curve shows calculated q dependence of $I(R=5\ \text{Å})/I(R=3.5\ \text{Å})$.

The introduction of defects by compression might seem surprising at first, since generally compression induces crystallization in molten materials. However, one should keep in mind that compression favors only compactness and not necessarily ordering. The melting of ice and the reentrance phenomenon in liquid crystals [8] are typical examples of such a behavior.

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