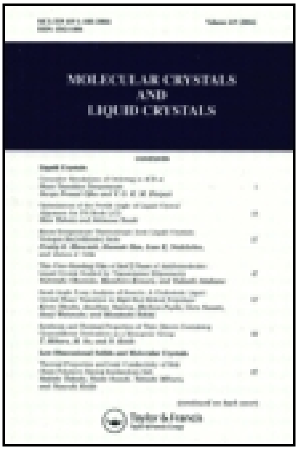

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X-Ray Diffraction Study on Discotic Lamellar Phase in Bis(1,3-di(p-n-alkoxyphenyl)propane-1,3-dionato)copper(II)

H. Sakashita [a] [c] , A. Nishitani [a] , Y. Sumiya [a] , H. Terauchi [a] , K. Ohta [b] & I. Yamamoto [b]

[a] Department of Physics, School of Science, Kwansei Gakuin University, Nishinomiya 662, Japan

[b] Department of Functional Polymer Science, Faculty of Textile Science & Technology, Shinshu University, Ueda 386, Japan

[c] Center of Advanced Instrumental Analysis, Kyushu University, Kasuga 816, Japan

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X-Ray Diffraction Study on Discotic Lamellar Phase in Bis(1,3-di(p-n-alkoxyphenyl)propane-1,3-dionato)copper(II)

H. SAKASHITA,† A. NISHITANI, Y. SUMIYA and H. TERAUCHI
Department of Physics, School of Science, Kwansei Gakuin University, Nishinomiya 662, Japan

and

K. OHTA and I. YAMAMOTO
Department of Functional Polymer Science, Faculty of Textile Science & Technology, Shinshu University, Ueda 386, Japan

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X-ray diffraction measurements have been carried out on bis(1,3-di(p-n-alkoxyphenyl)propane-1,3-dionato)copper(II) to clarify the detailed structural properties on the discotic mesophase. It is confirmed that the lamellar structure is realized in the discotic phase and the tilt angle of molecules to the layer is about 5°. The crystal-to-discotic phase transition occurs involving a large fluctuation of the inter-molecular distance along normal to the molecular plane within the layer. On the other hand, the transition from the discotic-to-isotropic liquid phase is characterized by the destabilization of the layer structure due to the randomizing of both the position and the orientation of molecules.

INTRODUCTION

Recently, "the discotic lamellar phase D_L" which is so far not included in categorized mesophases of disk-like molecules, i.e., the columnar phase and the discotic nematic phase, has been discovered in a series

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†Present address: Center of Advanced Instrumental Analysis, Kyushu University, Kasuga 816, Japan.

of disk-like complexes, bis(1,3-di(p-n-alkoxyphenyl)-propane-1,3-dionato)copper(II) (abbreviated as C_nO—Cu, n = 6 ~ 12).[1] The supercooled discophases of complexes from C_6O—Cu to $C_{12}O$—Cu at room temperature have shown the X-ray diffraction pattern characteristic of a lamellar (discotic smectic) structure: the spacings estimated from the position of Bragg reflections are exactly in the ratios 1:1/2:1/3:1/4. Furthermore, the miscibility tests between C_8—Cu and C_{10}—Cu or C_8O—Cu, where C_n—Cu (n = 1 12) represents the bis(1,3-di(p-n-alkylphenyl)propane-1,3-dionato)copper(II), have revealed that the discotic phase in C_8O—Cu is different from the *D* phase in C_8—Cu and the discotic phase in C_{10}—Cu,[2,3] and is a new discotic lamellar phase. Big broken fan-like textures have also been observed commonly in complexes from C_6O—Cu to $C_{12}O$—Cu. While these facts suggest that "the discotic lamellar phase" is realized in complexes from C_6O—Cu to $C_{12}O$—Cu, the detailed structural property has not been established. In this paper, we wish to report the result of the X-ray diffraction measurements on $C_{12}O$—Cu.

EXPERIMENTAL

$C_{12}O$—Cu was sealed in a copper cell (0.25 mm thick, 3 mm in diameter) or a Kapton cell (0.1 mm thick, 1 mm in diameter). The molecules were aligned by repeatedly heating to the isotropic liquid phase and cooling to the discotic phase. Figure 1 shows the schematic arrangement of the X-ray diffractometer system used. The molecular structure and the phase transition sequence of $C_{12}O$—Cu are shown below. $C_{12}O$—Cu has the lowest transition temperature in a series of complexes from C_6O—Cu to $C_{12}O$—Cu and is very suitable for the present experiment because both Kapton and mylar films cannot withstand high temperatures. The temperature of the sample was monitored by a copper-constantan thermocouple embedded in the sample and was stabilized within ±0.2°C.

An X-ray generator with a rotating copper anode loaded with 40 kV and 80 mA and the conventional double axes X-ray diffractometer attached with a χ-circle was employed for the X-ray diffraction measurements ($2\theta-\theta$). As the X-ray source, Cu-K_α radiation monochromatized by a pyrolytic graphite crystal was used. The X-ray beam at the sample was collimated to a size of 1×1 mm^2. Divergence slits of 0.5×0.6 mm^2 and receiving slits of 0.8×2 mm^2 were used to obtain the profiles of reflections.

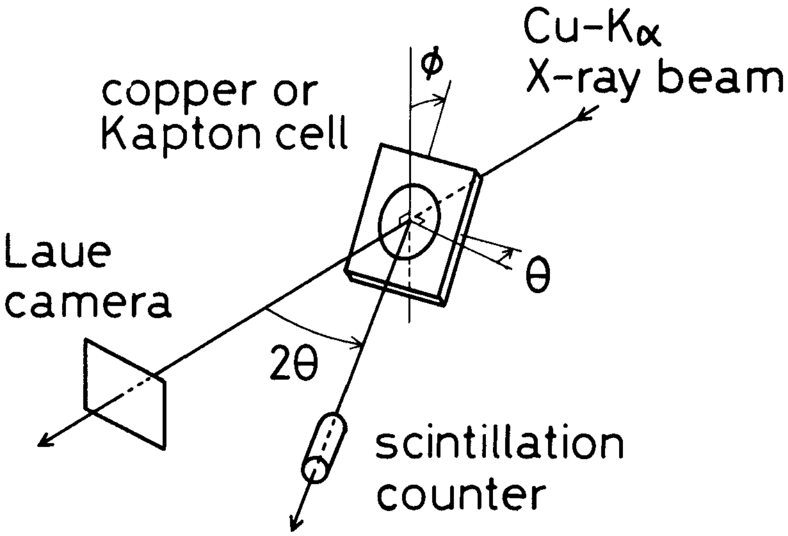
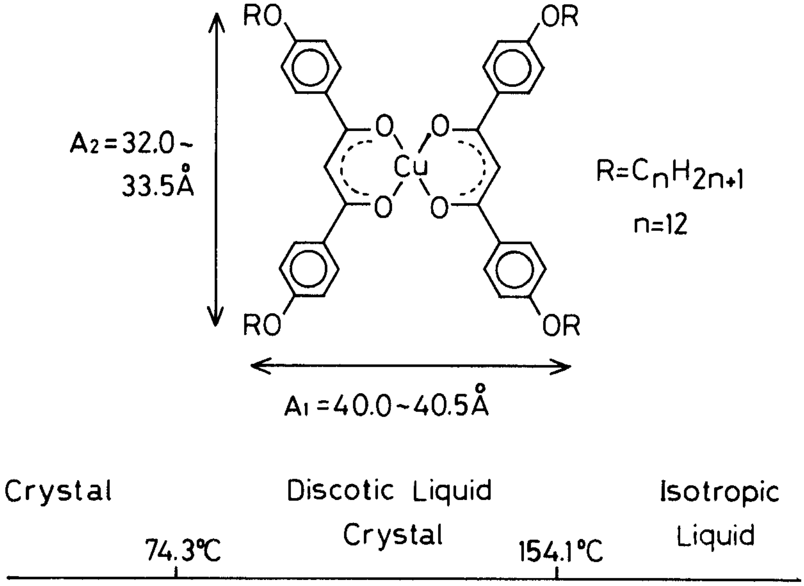


FIGURE 1 The schematic arrangement of the X-ray diffractometer system.



SCHEME 1

RESULTS

Figure 2(a) shows the typical Laue pattern of the discotic phase of $C_{12}O$—Cu in the case of $\theta = 0°$ and $\phi = 0°$ setting, where ϕ represents the azimuthal angle from the direction normal to the incident X-ray beam. Four peaks can be observed along the horizontal direction; these spacings are 32.8 Å, 16.0 Å, 10.4 Å and 7.8 Å, respectively. The ratio of these spacings are 1:1/2:1/3:1/4, which are explained in terms of a layer structure with an interlayer spacing of about 32 Å. This interlayer spacing is comparable with the molecular length A_2 (= 32.0 ~ 33.5 Å) calculated from the C.P.K. molecular model by Ohta *et al.*[1] On the other hand, fine peaks can be seen along the vertical direction; the spacings estimated are 45.3 Å, 11.9 Å, 5.9 Å, 5.4 Å and 4.1 Å, respectively. The spacing of 5.4 Å can be assigned to be the distance of alkoxy chains between the neighbouring molecules stacked along normal to the molecular plane within the layer,[4] while those of 11.9 Å and 5.9 Å cannot. The spacing of 45.3 Å is nearly equal to the molecular length A_1 (= 40.0 ~ 40.5 Å) as shown in the figure of the molecular structure. This suggests the contamination of the other domains; i.e. the domains with the same layer structure but with the different orientation of the layer. The peculiar feature of the Laue pattern (Figure 2(a)) is that two lines formed by connecting points of the maximum intensity of the peaks lying along the horizontal and the vertical direction do not cross each other with the angle of 90°. Therefore, this indicates the tilting of the molecular plane from the perpendicular direction to the layer. The tilt angle of the molecular plane to the layer is estimated to be about 5° to 100°C.

In order to check the existence of the columnar structure often seen in the discotic phase, Laue photographs were taken by setting ϕ-angle to 30°, 60° and 90° with θ-angle fixed at 0°. In these settings, the Bragg reflections which are indicative of the layer structure and observed along the horizontal direction show the same pattern as that of Figure 2(a), while the reflections observed along the vertical direction exhibit the diffusive arc-like pattern. This indicates that the molecules stack randomly within the layer and the columnar structure is not formed. Furthermore, the Laue photograph was taken at the setting of $\theta = 90°$ and $\phi = 0°$ as shown in Figure 2(b). The Bragg reflection caused by the layer structure disappears and instead the broad ring signifying the inter-molecular distance along normal and parallel to the molecular plane within the layer is observed; this confirms the liquid-like configuration of the molecules within the layer and the non-existence of the columnar structure. Figure 3(a) shows

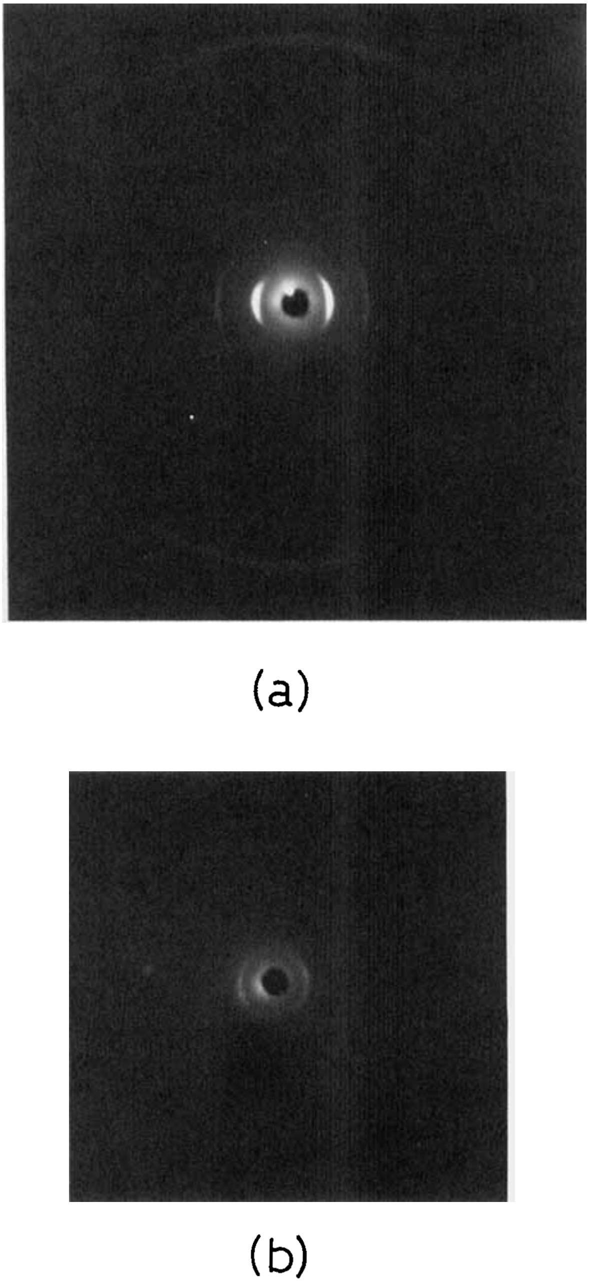


FIGURE 2 Laue photographs with angles set at θ = 0° and ϕ = 0° (a), and at θ = 90° and ϕ = 0° (b).

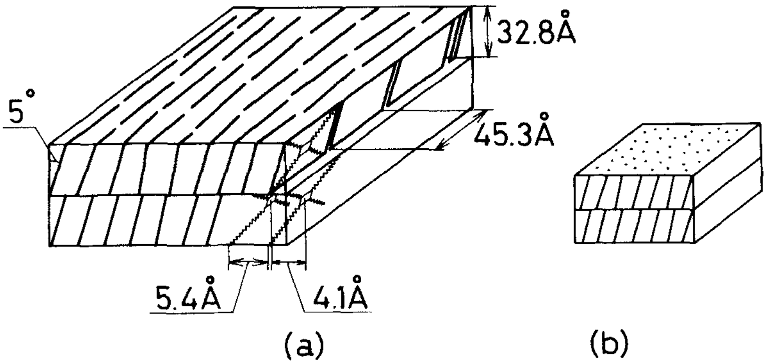


FIGURE 3 Schematic representations of the structures of (a) discotic lamellar phase (D_L) of $C_{12}O$—Cu, and (b) the classical smectic-C phase of rod-like molecules. The layer structure in (a) resembles that in (b).

the structure of the discotic lamellar phase deduced from the above examination. The structure is very similar to that of the smectic-C phase of the rod-like molecules as shown in Figure 3(b).

The temperature dependence of the peak intensities of the Bragg reflections which are indicative of the layer structure (●) and of the inter-molecular distance (▲) normal to the molecular plane in the layer are shown in Figure 4, respectively. Both intensities change continuously around the crystal (K)-to-discotic (D) transition temperature T_{KD} and decrease with increasing temperature. Above the discotic-to-isotropic liquid (I.L.) transition temperature T_{DI}, only the diffuse scattering reflecting the layer structure with the short-range correlation remains.

Figure 5 shows the temperature dependence of the full width at half maximum's (FWHM's) of the peak profiles along the $2\theta-\theta$ direction, where black circles (●) and black triangles (▲) represents the FWHM's of the corresponding Bragg reflections defined in Figure 4. The former FWHM (●) is constant in the *K* and *D* phases and shows no appreciable change around T_{KD}, and increases rapidly above T_{DI}. This suggests the fluctuation of the layer spacing becomes dominate only in the I.L. phase. On the contrary, the latter FWHM (▲) shows the critical increase around T_{KD} and T_{DI}; the fluctuation of the inter-molecular distance within the layer grows around both transition temperatures. In contrast to the behaviour of the FWHM's, the layer spacing and the inter-molecular distance exhibit no abrupt change around the T_{KD} as shown in Figure 6(a). The layer spacing increases monotonically in both *K* and *D* phases with increasing temperature. The inter-molecular distance along normal to the molecular plane within the layer increases gradually in the *K* phase and grows

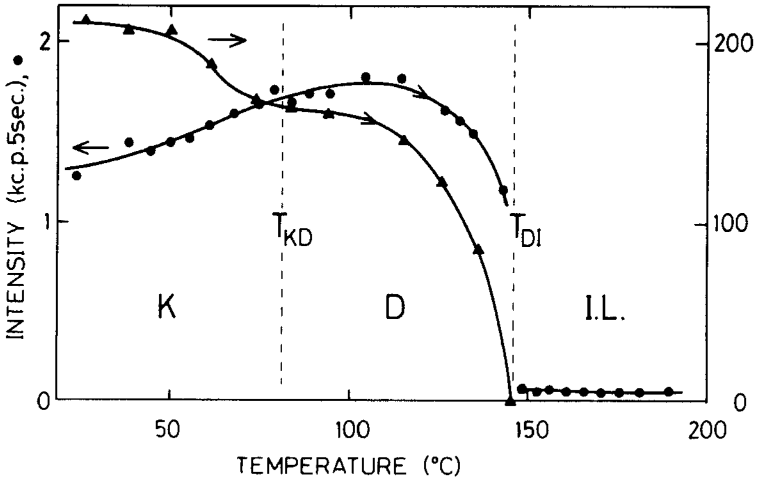


FIGURE 4 Temperature dependence of the peak intensities corresponding to the layer structure (●) and to the inter-molecular distance along normal to the molecular plane within the layer (▲).

furthermore in the *D* phase with increasing temperature. Therefore, it is concluded that the molecules in the layer stack more loosely in the *D* phase than in the *K* phase, though the layer structure is maintained rigidly in both phases in spite of the increase in the layer spacing. The loose stacking originates in the melting of alkoxy chains.

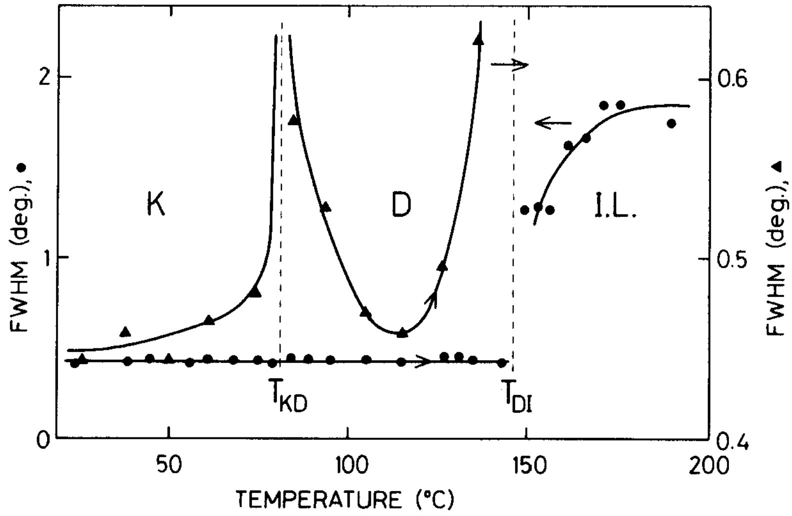


FIGURE 5 Temperature dependence of the full width at half maximum of peaks corresponding to the layer structure (●) and to the inter-molecular distance along normal to the molecular plane within the layer (▲).

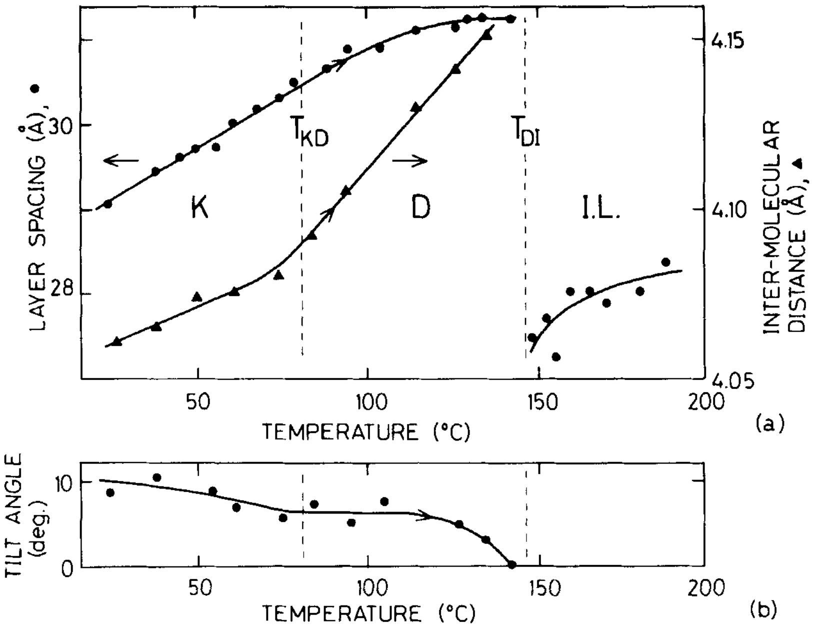


FIGURE 6 (a) Layer spacing (●) and the inter-molecular distance (▲) along normal to the molecular plane within the layer as a function of temperature. (b) Tilt angle vs. temperature.

On the other hand, the I.L. phase is characterized by the breakdown of the layer structure owing to the random configuration (both the position and the orientation) of the molecules. The other peculiar feature of the *D* phase is the tilting of the molecules to the layer, while the tilting is also observed in the *K* phase. Figure 6(b) shows the tilt angle of the molecules as a function of temperature, which is determined by taking the Laue photographs at each temperature and at the setting of $\phi = 0°$ and $\theta = 0°$. The tilt angle decreases with increasing temperature in both *K* and *D* phases; it exhibits no anomaly around T_{KD} and the tilting structure becomes extinct in the I.L. phase. The order-parameter-like behaviour of the tilt angle is analogous to that of the smectic-C phase of the rod-like molecule.

CONCLUSION

The present X-ray diffraction measurement confirmed that the discotic mesophase of $C_{12}O$—Cu forms the layer structure which is characterized by the tilt of the molecule to the layer and by the random positioning of the molecules within the layer, and no columnar structure. The *K*-to-*D* phase transition takes place involving the large fluctuation of the inter-molecular distance along normal to the molecular plane within the layer and maintaining the layer structure. On the other hand, the *D*-to-I.L. phase transition is caused by the enhancement of the disorder of the molecular position and orientation involving the destruction of the layer structure.

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