

## Hole Mobilities in Trivalent Metal Phthalocyanine Thin Films. 2. Anomalous Mobility Temperature Dependence in the Low-Temperature Region 213–93 K for Chloroaluminum, Chlorogallium, and Chloroindium Phthalocyanine Thin Films

A. Ioannidis and J. P. Dodelet\*

INRS-Énergie et Matériaux, C.P. 1020, Varennes, Québec, Canada J3X 1S2

Received: October 8, 1996<sup>®</sup>

In the first paper of the titled two-part study, the temperature and field dependencies of hole mobility in an upper temperature range of  $T_m = 333\text{--}213\text{ K}$  for ClAlPc thin films were determined as a function of structural organization using the time-of-flight technique. The present paper reports the results of mobility measurements on extending the measurement temperature range down to  $\sim 90\text{ K}$  in chloroaluminum (ClAlPc), chlorogallium (ClGaPc), and chloroindium phthalocyanine (ClInPc) thin films vacuum sublimed on substrates maintained at either  $T_s = 23$  or  $90\text{ }^\circ\text{C}$ . The mobility behavior undergoes an exceptional reversal in temperature dependence at low temperatures, beginning to rise on further cooling below  $\sim 200\text{ K}$ . The reversal is systematically studied, with mobility measurements as a function of temperature ( $T_m = 295\text{--}93\text{ K}$ ) and of field ( $E = 134\text{--}302\text{ kV/cm}$ ) at all temperatures and is shown to be widely reproducible. Mobilities at  $93\text{ K}$  equaled or surpassed their values at room temperature, with indicative high-field ( $E = 222\text{ kV/cm}$ ) values of  $7.9 \times 10^{-5}$ ,  $7.4 \times 10^{-5}$ , and  $7.25 \times 10^{-5}\text{ V/cm}^2$  for ClAlPc, ClGaPc, and ClInPc, respectively. The effect is reversible, with a hysteresis of several hours. The photocurrent transients themselves undergo a reversal in trends associated with temperature, their temporal profiles becoming comparable in the low-temperature region  $193\text{--}93\text{ K}$  with those observed at the higher temperatures. A color change with temperature is correlated to the mobility reversal. High-energy broadening in the absorbance spectra for all films combines with the mobility reversal to indicate a structural reorganization on lowering temperatures that causes greater overlap of the phthalocyanine macrocycles. Trends in mobility dependencies are shown to be consistent with the proposed increase in molecular orbital interactions. The temperature-induced nature of the reorganization is seen to preclude rigorous treatment of the mobility dependencies in the low-temperature range according to the mathematical formalism of disorder due to Bässler and co-workers. Qualitatively, however, the behavior of holes in ClAlPc-type materials remains explainable in terms of activated charge transport in the entire temperature range. Reversal of the mobility temperature dependence is not observed at low temperature for copper phthalocyanine.

### Introduction

The particular group of trivalent metal phthalocyanines composed of chloroaluminum, chlorogallium, and chloroindium phthalocyanine (Cl(M)Pc, where  $M = \text{Al, Ga, In}$ ) displays a number of interesting characteristics among pigments, most notably its high photoactivity and charge generation efficiency,<sup>1–5</sup> in addition to a strong absorbance in the visible. The latter has been shown to be very sensitive to the stacking patterns of the molecules, which determine the transition dipole interactions between adjacent chromophores.<sup>6a,7,8</sup>

Mobilities in phthalocyanine thin films have traditionally been deduced from space-charge-limited current techniques,<sup>6b</sup> deep trapping of carriers by molecular oxygen or impurities making time-of-flight (TOF) measurements difficult. However, in the case of ClAlPc, attention to purification and deposition procedures has allowed observation of TOF transients with various degrees of only moderate dispersivity throughout a full range of operational fields and temperatures.<sup>9</sup> In the first paper of the present two-part study, the mobility behavior was followed through a variation in organization of the ClAlPc films achieved by control of the substrate temperature,  $T_s$ , during deposition. The measurements performed in the temperature range  $T_m = 333\text{--}213\text{ K}$  were well described by a formalism for thermally activated carrier hopping within Gaussian distributions of site

energies and relative configurations, according to Bässler and co-workers.<sup>10–12</sup> A nondispersive-to-dispersive (ND–D) transition is predicted by the formalism at low temperatures, depending on film thickness and degree of disorder.<sup>13</sup> This transition is usually observed in the first few decades of the  $200\text{ K}$  range for the polymeric materials of comparable disorder widely studied (ref 14 and references therein), with thinner films causing larger transition temperatures. A deviation then at low temperatures from the dependencies predicted by the formalism is where most drift mobility measurements stop, as it identifies the ND–D transition. This is usually accompanied by a practical limitation, photocurrent transients becoming featureless when dispersive so that transit times can no longer be determined directly from the transient profiles.

However, transients did not become featureless either at or near the deviation obtained for the ClAlPc films previously reported. Furthermore, the size of the transient response under a given set of experimental parameters was still considerable and not obscured by noise. Therefore, mobility measurements could be extended to lower temperatures to investigate this unusual behavior. The unexpected phenomenon that was subsequently uncovered in the lower measurement temperature range  $T_m = 213\text{--}93\text{ K}$  forms the subject of the investigations reported in the present paper. The dependence of mobility on temperature will be seen to undergo a reversal at a temperature of  $\sim 200\text{ K}$ , beginning to rise with further cooling. The effect

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, January 15, 1997.

is accompanied by a host of observations relating to mobility and the transients themselves in ClAlPc and was confirmed to occur also in ClGaPc and ClInPc, but was notably absent in copper phthalocyanine. In all Cl(M)Pc materials the effect is accompanied by a correlated change in color. Q-band absorbance was measured as a function of temperature in order to track this color change. The spectroscopic indications toward the mechanism affecting mobility in the lower temperature range for the Cl(M)Pcs will be discussed in the context of a structural reorganization, after experimental pitfalls and alternative interpretations are considered. All measurements presented are for films of Cl(M)Pc similarly sublimed on substrates maintained at  $T_s = 23^\circ\text{C}$ . To determine whether the mobility reversal effect occurred for any different amount of structural organization than that produced by the particular deposition conditions used, measurements were also performed in ClAlPc films sublimed at  $T_s = 90^\circ\text{C}$  and throughout the full range of operational fields. This modest change in substrate temperature during deposition was previously shown<sup>9</sup> to yield a less disorganized amorphous film accompanied by a large increase in mobility. In the present study, the mobility reversal was obtained for the ClAlPc films sublimed at both maintained  $T_s = 23$  and  $90^\circ\text{C}$ , extending the range of experimental parameters for which the reversal effect is observable. Meanwhile, comparisons between field dependencies at different low temperatures in the present study will be largely qualitative, untreatable by the mathematical formalism based on disorder.

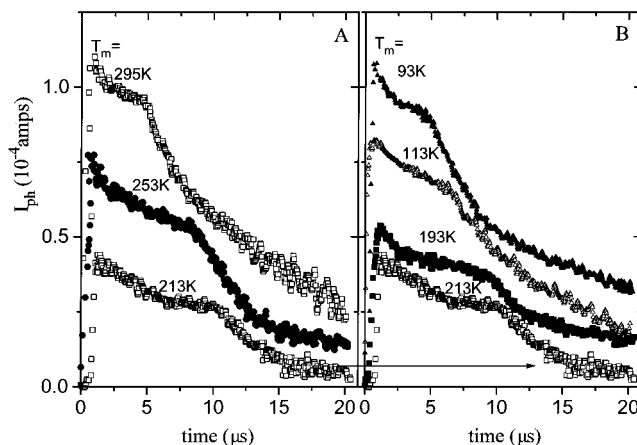
## Experimental Section

**A. Materials: Synthesis and Purification.** ClAlPc, ClGaPc, and ClInPc were prepared according to a procedure similar to that described by Owens and Kenny.<sup>15</sup> Actual synthesis and purification conditions as well as elemental analyses have been previously reported.<sup>5</sup> CuPc was purchased from Aldrich and purified according to the same procedure as Cl(M)Pcs.

**B. Sample Preparation.** For mobility measurements, 0.9–1.0  $\mu\text{m}$  thick films of the phthalocyanines were incorporated in a sandwich cell structure as described previously.<sup>9</sup> As a special precaution in comparing samples from different materials, the film thickness was maintained as nearly constant as was possible. Similarly, the sublimation rate was consistently  $\sim 1800$   $\text{\AA}/\text{min}$ , and the substrate was held at  $T_s = 23^\circ\text{C}$  for all the materials, except for ClAlPc, which was also deposited at  $T_s = 90^\circ\text{C}$ .

For absorbance measurements, 4000  $\text{\AA}$  thick samples of the Cl(M)Pcs were sublimed onto Al-covered glass substrates at  $T_s = 23^\circ\text{C}$  and with the same deposition rate of 1800  $\text{\AA}/\text{min}$ . Under the same conditions, ClAlPc was also sublimed onto plain glass substrates as well as glass covered with indium tin oxide (ITO) to compare for a possible effect of a conductive substrate on the Pc film.

**C. Measurements.** Mobility measurements were performed on the Cl(M)Pcs and CuPc thin films using the time-of-flight technique previously detailed (ref 9 and references therein). Logarithmic representations of the transients were used for transit time determination throughout the measurements, although usually a clear step or even a plateau was observed in the temporal transient profiles, as will be seen in the Results section. The range of applicable fields was limited at the high end by the resolution of the experimental arrangement or dielectric breakdown and at the low end by noise. The range of applicable temperatures was limited at low temperatures only by experimental capabilities, a temperature of 90 K being easily sustainable, while 80 K was obtainable but not for prolonged periods. Measurements of mobilities as a function of temper-



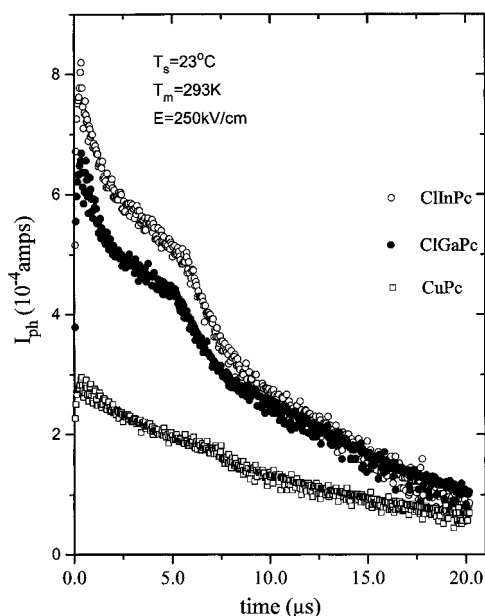
**Figure 1.** Comparison of photocurrent transient temporal profiles throughout a 200 K range of mobility measurements for a ClAlPc film of 0.9  $\mu\text{m}$  thickness sublimed at  $T_s = 23^\circ\text{C}$ . The applied field was 220 kV/cm. (A) Decreasing transients in the upper temperature range  $T_m = 295$ –213 K. (B) Reversal of temporal profile trends in the lower temperature range  $T_m = 213$ –93 K.

ature as well as of mobility versus field as a function of temperature were repeated twice on any given sample.

Absorbance measurements were performed on Cl(M)Pcs in transmission mode, in the wavelength range  $\lambda = 400$ –900 nm. The samples were enclosed in a vacuum chamber similar to that used in mobility measurements ( $\sim 10^{-3}$  Torr), custom-fit to a Hitachi Model 100–60 spectrophotometer. The same sample mount and temperature control system as those for mobility measurements were employed. Spectra were obtained in the temperature range 295–93 K for the phthalocyanine thin films as well as for their substrates alone, allowing for a minor baseline correction.

## Results

Figure 1A,B compares transients obtained at one field in the two temperature ranges  $T_m = 295$ –213 K and  $T_m = 213$ –93 K, respectively, for a ClAlPc film deposited on a substrate held at  $T_s = 23^\circ\text{C}$ . As in the companion paper, all temperatures of measurement,  $T_m$ , will be reported in units of degrees Kelvin, while the temperature at which substrates were held during film sublimation,  $T_s$ , will be reported in degrees Celsius as an aid to readability. Measurements were taken every 20 K, while a total of only seven transients are shown for clarity. The height of transients on lowering the temperature remained considerable so that noise is not a limiting factor even at 93 K, as can be seen in Figure 1B. Results in the “upper” temperature range 295–213 K followed the expected activated hopping behaviour, with transit times increasing and transient height decreasing as the temperature falls. However, on lowering the temperature further, a complete reversal of trends was observed, discernible in Figure 1B. Transit times decreased continuously in the lower temperature range, giving mobilities that increased with falling temperatures. Furthermore, the transient at 93 K looks very similar to that at 295 K, and the transit time determination is just as clear, yielding 4.9 and 5.0  $\mu\text{s}$ , respectively. The large extent of the temperature effect on transit time quickly eliminates the possibility that a contraction of the sample during cooling might account for the decrease in transit time. Thus for example, in the 100 K interval between 193 and 93 K, the thickness of the sample would have had to decrease by a factor of 2 in order to produce the observed transit time decrease from 9.6 to 4.9  $\mu\text{s}$ . The temperature at which the trends reversed their behavior, 193 K, was also marked by the beginning of a color change visible in the samples. The blue phthalocyanine

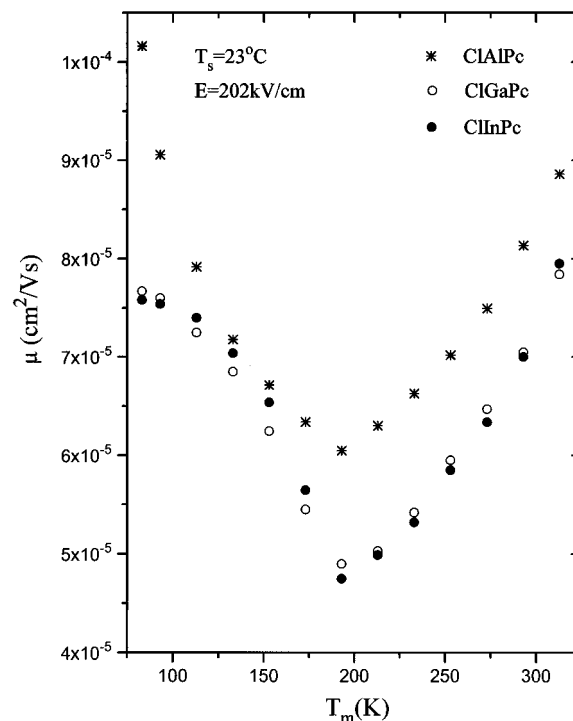


**Figure 2.** Comparison of transient profiles for similarly sublimed films of ClGaPc, ClInPc, and CuPc under the same experimental conditions of field and temperature.

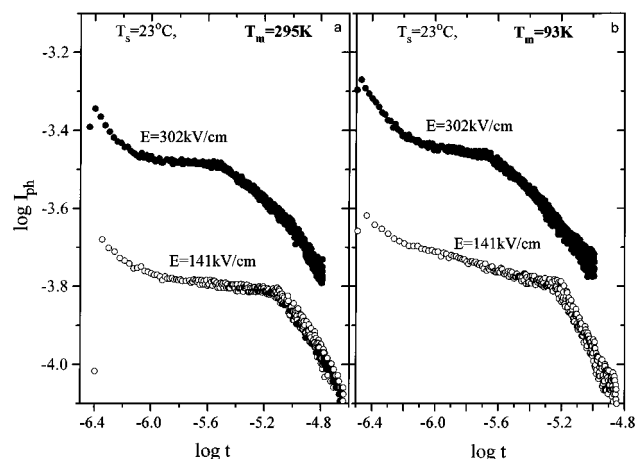
gradually acquired a violet hue. There is a distinction regarding the reversibility of results between the upper and lower temperature ranges above. While one could scale up and down in temperature without hysteresis for temperatures down to  $\sim 213$  K, the same is not true on attaining the lower temperatures. After reaching 93 K, there was a significant hysteresis effect when samples warmed back up to room temperature. Transients required up to 10 h to completely recover their original features. Once room-temperature transients were deemed identical to the original, the measurements were repeated on any given sample. There was no discernible difference between the two consecutive series of results.

The possibility that the effect might be shared by the other closely related Cl(M)Pcs was explored by a series of mobility measurements as a function of temperature in ClGaPc and ClInPc. For comparison, measurements were also performed on copper phthalocyanine (CuPc). Transients obtained for CuPc, ClGaPc, and ClInPc can be compared in Figure 2 at  $T_m = 23^\circ\text{C}$  for similarly deposited films on substrates held at  $T_s = 23^\circ\text{C}$ . The transients for ClGaPc and ClInPc do not break as sharply as those of ClAlPc in similarly prepared samples of the same thicknesses, but transit times are still easily obtainable. On the other hand, the temporal profile of CuPc transients was quite dispersive at the highest temperatures and the dispersion increased as the temperature was lowered. Eventually therefore, even the log-log representation, by which a transit time can usually be determined on dispersive transients,<sup>16</sup> yielded a smooth curve.

The mobilities determined from transients at the same field for a 230 K range of measurement temperatures are shown in Figure 3 for similarly deposited Cl(M)Pc films. As can be seen, the reversal in the trend of mobilities with temperature is apparent in all three Cl(M)Pc films, occurring at approximately the same temperature,  $\sim 190$  K. At the lowest temperatures that could consistently be maintained, 113–83 K, the mobilities for all three samples approached or even surpassed those at 295 K. As for CuPc, the range of measurements was limited, as a transit time could not be reliably determined below  $\sim 140$  K due to the increasingly dispersive transients mentioned above. Mobility values for CuPc ranged from  $\sim 3 \times 10^{-5}$  to  $7 \times 10^{-6} \text{ cm}^2/(\text{V s})$  at 313 and 143 K, respectively. However, this film clearly



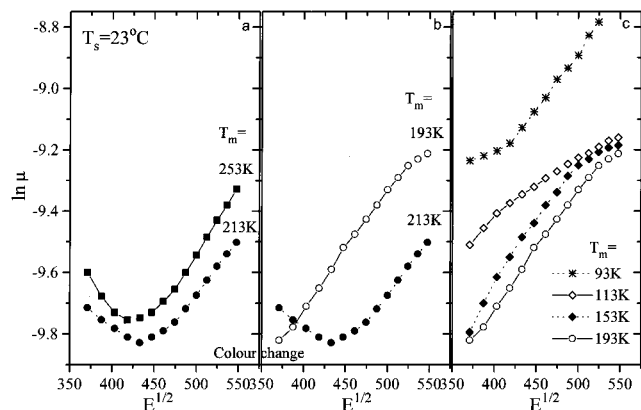
**Figure 3.** Mobility temperature dependence at constant field for similarly sublimed films of ClAlPc, ClGaPc, and ClInPc.



**Figure 4.** Comparison of logarithmic representation of transients parametric in field at  $T_m = 295$  and  $93$  K for a ClAlPc film deposited at  $T_s = 23^\circ\text{C}$ .

did not exhibit a reversal in mobility behavior within the temperature range investigated.

Finally, the charge transport behavior in the low-temperature region was investigated as a function of field and of film organization according to the rationale outlined in the Introduction. Mobilities were determined over a range of fields for ClAlPc films on substrates held at  $T_s = 23^\circ\text{C}$  and  $T_s = 90^\circ\text{C}$ , in order to ensure a range of reproducibility of the mobility reversal effect. Figure 4a,b compares two transients in logarithmic representation spanning the field range investigated at  $T_m = 295$  and  $93$  K, respectively, for a ClAlPc sample deposited on a substrate at  $T_s = 23^\circ\text{C}$ . The transit time determination is clear at all fields and at both 295 and 93 K. The logarithmic representation demonstrates a time-independent region just before the break in slope everywhere in the applicable field range and throughout the temperature range investigated. This establishes an only moderate dispersivity of transients throughout the entire field range studied and reinforces the comparability of measurements at both high and low temperature, as consid-



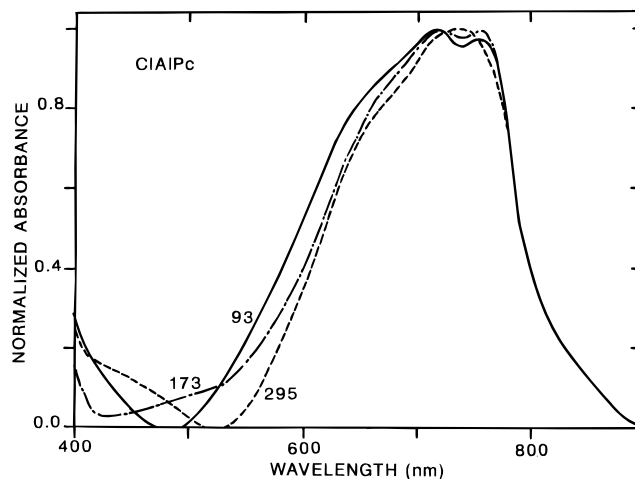
**Figure 5.** Comparison of the field dependencies of the mobility on cooling through the mobility reversal temperature for CIAIPc film deposited at  $T_s = 23$  °C.

ered in the Discussion section. Similarly clear transients were obtained for CIAIPc films deposited at the higher substrate temperature  $T_s = 90$  °C.

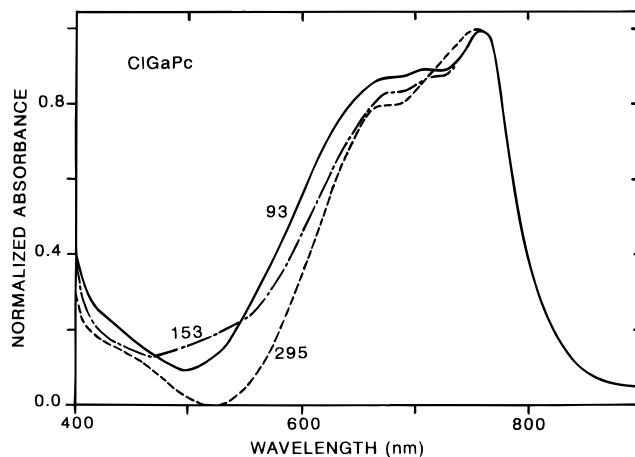
The mobilities obtained from such transients for CIAIPc deposited at  $T_s = 23$  °C are shown in Figure 5a,b,c over the temperature range  $T_m = 253$ –93 K. The operational field range was  $E = 122.5$ –302.5 kV/cm. Results are shown in semi-logarithmic form versus  $E^{1/2}$  and are separated into three plots, on the same scales in each plot, for comparison. The first plot (Figure 5a) illustrates the typical activated charge transport behavior at the higher temperatures, where mobility decreases with decreasing temperature. A linear dependence of  $\ln \mu$  versus  $E^{1/2}$  at the high fields is observed down to  $T_m = 213$  K, as usual.<sup>9</sup> The main, prominent observation on further lowering the temperature is that the mobility trend reversed throughout the applicable field range. The mobility reversal is highlighted in Figure 5b, where higher mobilities are observed at 193 compared to 213 K, initially at all but the lowest field values. An accompanying color change began to appear between 213 and 193 K. The ascending trend in mobility values is seen to continue in Figure 5c and extends to apply to all the observable fields in the low-temperature range 193–93 K. Secondary, more subtle differences in the mobility behavior at low  $T_m$  were also observable. The form of the mobility dependence on field changed at the same temperature, 193 K, where the mobility trend reversed. The low-field behavior became a roughly monotonic increase of mobility with field at even the lowest operational fields. This form applies throughout the low- $T_m$  range, with varied slope, as can be seen in Figure 5c. Finally, the temperature interval 113–93 K was marked by a more abrupt increase in mobility throughout the field range applied. The type and extent of conclusions derivable from such observations will be considered in the discussion.

Mobility measurements were also performed for a CIAIPc film deposited at  $T_s = 90$  °C over a field range of  $E = 62.5$ –225.63 kV/cm<sup>2</sup> from  $T_m = 295$ –93 K. The mobility reversed its decline on lowering temperatures below 233 K, giving a mobility value at 93 K that was comparable to that at 260 K. The continuous rise of the mobility saturates at the temperatures 113–93 K for the film at  $T_s = 90$  °C, unlike the films at  $T_s = 23$  °C. However, the same main observations hold; the mobility reversal, accompanied by a similar color change, being confirmed in this film sublimed with a greater structural organization at  $T_s = 90$  °C.

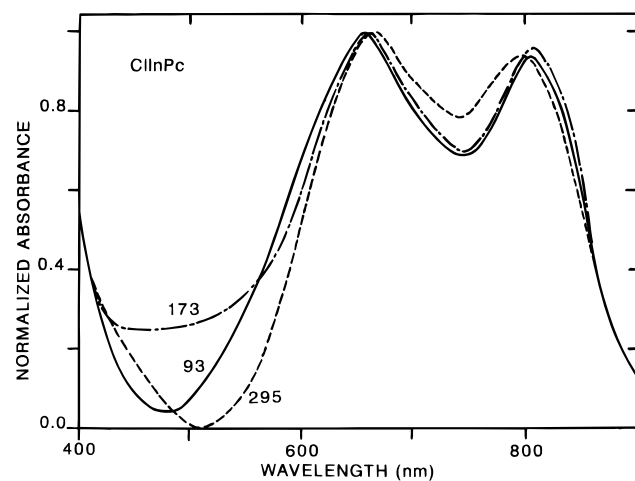
As far as the color of films is concerned, a distinct change was easily visible at around  $\sim 200$  K for ClGaPc and ClInPc, similar to the observation for CIAIPc. Conversely, for CuPc no color change was observed on cooling down to 80 K. The



**Figure 6.** Q-band absorbance measured at 93, 173, and 295 K for CIAIPc.



**Figure 7.** Q-band absorbance measured at 93, 153, and 295 K for ClGaPc.



**Figure 8.** Q-band absorbance measured at 93, 173, and 295 K for ClInPc.

change in colour was investigated by measuring the Q-band absorbance from 293 to 93 K of the three Cl(M)Pcs. The results are shown in Figures 6, 7, and 8 for 4000 Å thick films on Al-covered glass substrates of CIAIPc, ClGaPc, and ClInPc, respectively. Further measurements of CIAIPc on ITO-covered glass and on plain glass gave essentially the same results. Results were obtained at every 20 K and showed nearly no change in the absorbance profiles down to  $T_m = 213$  K for any of the Cl(M)Pcs. For each of the materials, three absorbance

spectra are shown that highlight the differences observed on decreasing temperature. The results at the three  $T_m$  shown are normalized to better compare the changes occurring in the absorbance profiles depicted.

The evolution of Cl(M)Pc absorbances with temperature are similar: (i) spectral features are better resolved by lowering the temperature (see for instance ClAlPc and ClInPc at around 735 nm); (ii) the absorbances throughout the temperature range coincide for the red side of the Q-band, while from 193–93 K there is a distinct broadening of the Q-band blue side; (iii) with lowering temperature, there is an initial increase of the absorbance in the 510 nm region, followed by a decrease as the temperature is lowered further.

The possibility of a phase transition was investigated by differential scanning calorimetry (DSC). Samples of the three Cl(M)Pcs were tested in both powder form and as thin films deposited directly on the DSC aluminum sample holders. Smooth curves were obtained for all samples, irrespective of the rate or sign of the change in temperature. There was no spike, step, or discontinuous change in slope to mark a distinct phase transition in the temperature range investigated (77–295 K).

## Discussion

**A. Meaningful Drift Mobilities.** The first consideration when discussing results of the time-of-flight measurements below  $T_m = 213$  K is whether they can be compared to results at higher temperatures. At issue is whether the transit times obtained from low-temperature transients are meaningful within the context of drift mobility studies. The issue arises both from theoretical predictions based on the disorder formalism, as well as a variety of experimental results showing a transition to dispersive transients with decreasing heights as temperatures decrease. The description of a dispersion transition by the formalism is of interest in the present work, as the disorder model has been shown to closely predict the mobility behavior in variously deposited thin films of ClAlPc in an  $\sim 100$  K range of temperatures (333 to  $\sim 233$  K).<sup>9</sup>

According to simulations in the formalism, the transient outline is expected to become a smooth, featureless decay as temperatures fall, no longer indicating the transit time by a plateau or any knee that would mark arrival of the charge packet at the blocking contact. Such a transient is considered to mark the transition to a dispersive charge transport regime where the charge carrier packet does not equilibrate during its transit through the film.<sup>13,17,18</sup> Interactions with deeper trap levels also become increasingly important as temperature decreases. The effect is dependent on film thickness; the shorter the length that carriers have to traverse, the higher the temperature at which the transit becomes dispersive. In a logarithmic representation of the transients, the transition to truly dispersive transport is marked by the vanishing of a time-independent region in the logarithmic profile, according to simulations. Transients may however, at whatever temperature, appear moderately dispersive, due to structural disorder, nonthermal field-induced broadening of the carrier packet, and/or complications from a relatively small concentration of traps. The transit times derived from moderately dispersive transients give mobilities that are thickness independent and still representative of bulk transport.<sup>18</sup> However, as temperature continually decreases, the mobilities operationally defined from increasingly dispersive transients should become less and less representative of bulk properties. Comparison then to those at higher temperatures would have limited meaning.

The issue of comparability is resolved on considering the temporal profiles depicted in Figure 1 in a 200 K range of

measurement temperatures for ClAlPc deposited on a substrate held at  $T_s = 23$  °C. While transients are broadened, they can be said to improve with lowering temperature past a minimum at 213 K as they then recover the profiles observed at higher temperatures. The mobility determination in the lower temperature range 213–93 K is therefore comparable to that in the upper range 295–213 K. The ensuing increase in mobility with decreasing temperatures in the low-temperature range is therefore meaningful and quite dramatic. Similarly clear results were obtained for the other Cl(M)Pcs (Figures 2, 3) and throughout the whole operational field range, demonstrated for ClAlPc in Figures 4 and 5, as well as for ClAlPc differently sublimed at  $T_s = 90$  °C. No mobility reversal was seen for CuPc, which furthermore displayed rather featureless transients (Figure 2). It may also be noted that a deviation at  $\sim 233$  K from the disorder formalism's description that was previously observed in ClAlPc films does not seem likely therefore to be due to a dispersive transition. Rather, it could be considered to signal the operation of an underlying temperature-related mechanism affecting mobility in the Cl(M)Pcs.

**B. Anomalous Mobility-Behavior: Two Untenable Explanations.** With decreasing temperature, the mobility behavior first deviates from the description of the disorder formalism, then reverses its decline and continually rises below a temperature of  $\sim 190$ –200 K. When considering the field-dependent mobilities of ClAlPc at different measurement temperatures in Figure 5, it is seen that the field dependencies vary considerably from temperature to temperature in the low-temperature range. Therefore, the particular form of a mobility temperature dependence at a constant field depicted in Figure 3 will depend on the particular field chosen. At the same time however, Figure 5 serves to demonstrate that the mobility reversal is not a spurious event, as a very clear general trend of increasing mobility with lowering temperature exists throughout the entire field range applicable.

Associated with the increase in mobility at low temperatures is a color change. This is tracked throughout the  $\sim 200$  K temperature range investigated in the absorbance results of Figures 6–8 for all three Cl(M)Pcs. A Q-band broadening toward blue, which begins near the temperature at which mobilities stop decreasing and start rising, is evident for all Cl(M)Pcs. The mechanism therefore that will account for the mobility increase in the low-temperature range must also account for the blue broadening of the Q-band observable in Cl(M)Pc samples in the same range. A second observation concerning color change is the transitional increase in absorbance at wavelengths around 510 nm, which is shown for all Cl(M)Pcs in Figures 6–8. It marks the beginning of color changes in the films, peaks early at a temperature just below the mobility reversal, and is no longer seen by the minimum temperature 93 K.

The transitory nature of this “green” absorbance serves to eliminate one possible temperature-related effect as the cause of the mobility increase. Indeed, potential trap filling when lowering temperature was considered among the possibilities for causing an increase in mobility. Filling deeper traps may effectively eliminate slower charge transport routes. There exists documented evidence that positive macrocycle ions (filled traps) may absorb in the 500 nm wavelength range.<sup>19–23</sup> However, such a mechanism may be expected to result in a detectable space-charge effect on the transients as the ions would increasingly distort the applied field. No such effect was ever detected at any temperature, while the usual precaution of short-circuiting samples under a brief light pulse barrage was taken between measurements. Furthermore, if filled traps were

the cause of a "green" absorbance appearing at temperatures near the mobility reversal ( $\sim 200$  K), an emptying of traps would have to be concluded from the disappearance of this absorbance on further lowering temperatures (93 K). This mechanism then becomes untenable.

A second interpretation of any inverse mobility dependence on temperature involves coherence: if transport became coherent at  $\sim 200$  K, then decreasing temperature would be expected to decrease phonon scattering and so improve mobility. The main difficulty with this interpretation is that coherent transport is implausible given mobility values on the order of  $10^{-5}$  cm<sup>2</sup>/(V s).

**C. Anomalous Mobility Behavior: A Substantiated Explanation.** Such conceptual difficulties are not encountered if the overall absorbance changes linked to the mobility trend reversal, in conjunction with the significant hysteresis, are considered to indicate *a gradual and reversible type of structural reorganization*. The changing structure would affect intermolecular interactions and thereby affect mobility. Such a mechanism furthermore permits retaining the activated nature of charge transport for the materials studied, notwithstanding the apparently contrary indication of a mobility that varies inversely with temperature.

Cl(M)Pcs single crystals are thought to crystallize in a triclinic structure with molecules stacking along the *c*-axis. The planes of the Pc macrocycles lie parallel to each other and are displaced in *a* and *b* directions (slip-stack) with Cl pointing alternately up and down along the *c*-axis.<sup>24</sup> The triclinic structure is detected for partially polycrystalline ClAlPc films sublimed on substrates held at  $T_s = 23$  and  $90$  °C.<sup>5,25</sup> Other intermolecular configurations have been found for ordered Cl(M)Pc thin films grown by molecular beam epitaxy (MBE).<sup>26–28</sup> These indicate that a cofacial packing of molecules (which corresponds to the greatest area of macrocycle overlap) produces an absorbance spectrum that is shifted and/or broadened toward blue when compared to slipped stacking. Apart from the MBE grown films of Cl(M)Pcs mentioned above, a blue shift has also been noted in comparing ClAlPc films formed by sublimation on NaCl substrate with ClAlPc formed on quartz.<sup>29</sup> This was associated with a monoclinic, compared to a triclinic, phase. The proposed explanation for an absorbance blue shift derives from exciton theory<sup>7</sup> as applied to aggregates of small chromophores.<sup>8</sup> The sensitivity of the absorbance to transition dipole interactions is well-known in Pcs.<sup>6a</sup> Parallel orientations of molecular transition dipoles in a cofacial arrangement yield higher energy transitions compared to other types of orientations, such as head-to-tail or oblique. In comparing absorbance spectra of Cl(M)Pc solids, the extent of ordering necessary for changes in orientation and degree of macrocycle overlap to be detectable is considered to be only on the order of 5–10 molecular units.<sup>28</sup> Such short-range order is certainly possible in the thin films sublimed in the present study on substrates held at  $T_s = 23$  and  $90$  °C.<sup>5,25</sup>

A horizontal shifting of molecular planes toward greater overlap may then be envisioned on lowering temperature, as the lattice may be expected to contract. A larger area of overlap in horizontally stacked macrocycles would be at the origin of the absorbance broadening toward blue. It would also increase the  $\pi$ – $\pi$  interactions<sup>30</sup> which are thought to aid charge transport. Such an effect is indeed considered responsible for improved charge transport in certain discotic liquid crystals, notably in the highly ordered discotic helical mesophase of 2,3,6,7,10,11-hexahexylthiotriphenylene.<sup>31</sup> For this material it was also noted that large effects on charge transport in the bulk can be produced by very small changes in relative molecular orientations. Thus, while differences in mobility and absorbance were observed in

the present study, the smooth DSC result mentioned in the previous section may simply reflect an energy of transition too small to be detected. CuPc, having a different crystallization tendency than Cl(M)Pcs to begin with (usually the  $\alpha$  form for vacuum-sublimed films<sup>32</sup>), does not display the unusual mobility behavior shown by all Cl(M)Pcs studied in this work.

Fundamental consequences of the increased molecular overlap, especially in relation to plausibility, are briefly considered below. The assumption of transport site localization that is central to hopping transport results from the weak nature of intersite interactions. At a large enough value of intermolecular interactions, coherent transport would be expected to occur. However the largely amorphous nature of the films presently considered means that any cooling-induced increase of molecular overlap is still far from achieving such a regime. That the mobility in these mostly amorphous solids behaves unexpectedly is perhaps only due to the density of macrocycles achievable in Cl(M)Pc films which brings the molecular planes within proximity of the van der Waals distance, in comparison with the more dilute hopping systems of, for example, molecularly doped, pendant, or main-chain polymer films in which mobility has been widely studied and modeled.<sup>14,33,34</sup> Of relevance in the present work may be the spatial correlation effects postulated by Gartstein and Conwell,<sup>35</sup> affecting, among others, systems with short-range order. A consequence of such correlation is that the usually observed high-field Poole–Frenkel-type mobility dependence ( $\ln \mu \propto E^{1/2}$ ) is extended over a wider field range. This is indeed seen in Figure 5b,c in the low-temperature range for a ClAlPc film at  $T_s = 23$  °C. Such an explanation then of the change in mobility field dependence observed would imply an increased spatial correlation of transport sites (Pc macrocycles) at low temperatures, which is just the situation obtainable according to the structural reorganization discussed above. On the other hand, effects related to the disorder present in the Cl(M)Pc films are difficult to extract during a structural reorganization that is caused by temperature change, as is the case here. This is due to the fact that necessary disorder parameters are obtained specifically from the temperature dependencies of the mobility in a particular material structure. In the present case, a continuous change in structure is thought to result, below 213 K, at each changing temperature, making a quantitative treatment according to the formalism of disorder impossible. Qualitatively however, the behavior of holes in ClAlPc-type materials remains explainable in terms of activated charge transport in the entire temperature range studied.

## Conclusion

Hole mobilities in ClAlPc, ClGaPc, and ClInPc have been systematically shown to undergo a reversal in their temperature dependence at low temperatures. The mobility rises continually on cooling from 193 to 93 K in films of all three Cl(M)Pcs similarly deposited on substrates maintained at  $T_s = 23$  °C during deposition. The same results are obtained with  $T_s = 90$  °C. The reversal effect is gradual but at the same time outstanding, the mobility regaining or surpassing its value at room temperature by the end of the temperature variation at 93 K. The trends of the temporal features of the photocurrent transients undergo a concomitant reversal in temperature dependence, becoming comparable in the low-temperature range to those at higher temperatures. The mobility reversal effect was shown to apply throughout the entire range of applicable fields in ClAlPc, whose charge transport had been extensively studied at temperatures above 213 K, in the companion paper, for thin films of varied structural organization. A color change visibly occurring in all samples was investigated by measure-

ments of Q-band absorbance as a function of temperature. The overall result of the temperature variation on the absorbance spectra of all three Cl(M)Pcs was a significant blue broadening. The combined results from mobility and absorbance measurements are shown to indicate the operation of a temperature-induced structural reorganization effect. Based on literature results, it is proposed that the reorganization is a shift toward greater phthalocyanine macrocycle overlap of the Cl(M)Pcs, whose molecules tend to form close-packed face-to-face configurations. The increased area of overlap yields greater  $\pi$ -orbital interactions, giving a net effect of increased mobility with decreasing temperature. The proposed explanation for rising mobilities with lowering temperatures retains the concept of hopping-controlled hole transport. However, the temperature-induced nature of the structural change has as a consequence that the mobility dependencies in the low-temperature region cannot be rigorously treated by the mathematical formalism due to Bässler and co-workers, which describes disorder-controlled hopping very well in CIAIPc at higher temperatures. The low-temperature anomalous mobility dependence described for Cl(M)Pcs is not a general trend in phthalocyanines. Indeed, it is not observed in CuPc, which is known to be of a different structural organization from Cl(M)Pcs. It would be interesting to study the hole mobility behavior of oxotitanium phthalocyanine, a molecule of architecture similar to Cl(M)Pcs, which also displays high photoactivity and various polymorphic structures.<sup>36–41</sup>

**Acknowledgment.** The authors would like to thank Zoran Popovic, Andrew Melnyk, and Paul Borsenberger, as well as Larry Schein and David Dunlap for insightful discussions of the results. We are indebted to Roland Côté for the synthesis of Cl(M)Pc and to Gerald Perron for patient aid with the DSC measurements. This work was supported by the National Science and Engineering Research Council of Canada.

## References and Notes

- (1) Loutfy, R. O.; Hor, A. M.; Di Paola-Baranyi, G.; Hsiao, C. K. *J. Imaging Sci.* **1985**, 29, 116.
- (2) Loutfy, R. O.; Hor, A. M.; Rucklidge, A. *J. Imaging Sci.* **1987**, 31, 31.
- (3) Popovic, Z. D.; Hor, A. M. *Proc. SPIE (Fluorescence Detection II)* **1988**, 910, 168.
- (4) Melnyk, A. R.; Pai, D. M. *Proc. SPIE (Hard Copy Print Mater., Media, Processes)* **1990**, 1253, 141.
- (5) Santerre, F.; Côté, R.; Veilleux, G.; Saint-Jacques, R. G.; Dodelet, J. P. *J. Phys. Chem.* **1996**, 100, 7632.
- (6) Simon, J.; André, J.-J. *Molecular Semiconductors*; Springer Verlag: Berlin, 1985; (a) p 93; (b) p 110.
- (7) Davydov, A. S. *Theory of Molecular Excitons*, Nauka Press: Moscow, 1968.
- (8) Kasha, M. In *Spectroscopy of the Excited State*; DiBartolo, B., Ed.; Plenum Press: New York, 1976; pp 337–363.
- (9) Ioannidis, A.; Dodelet, J. P. *J. Phys. Chem. B* **1997**, 101, 891.
- (10) Movaghar, B.; Grünewald, M.; Ries, B.; Bässler, H.; Wurtz, D. *Phys. Rev. B* **1986**, 33, 5545.
- (11) Richert, R.; Bässler, H.; Ries, B.; Movaghar, B.; Grünewald, B. *Phil. Mag. Lett.* **1989**, 59, 95.
- (12) Bässler, H. *Phys. Status Solidi* **1993**, B175, 16.
- (13) Movaghar, B. *J. Mol. Electron.* **1988**, 4, 79.
- (14) Borsenberger, P. M.; Weiss, D. S. *Organic Photoreceptors for Imaging Systems*; Marcel Dekker: New York, 1993.
- (15) Owens, J. E.; Kenney, M. E. *Inorg. Chem.* **1962**, 1, 331.
- (16) Scher, H.; Montroll, E. W. *Phys. Rev.* **1975**, B12, 2455.
- (17) Borsenberger, P. M.; Magin, E. H.; van der Auweraer, M.; de Schryver, F. C. *Phys. Status Solidi* **1993**, 140a, 9.
- (18) Bässler, H. *Phys. Status Solidi* **1993**, B175, 16.
- (19) Dolphin, D.; James, B. R.; Murray, A. J.; Thornback, J. R. *Can. J. Chem.* **1980**, 58, 1125.
- (20) Muralidharan, S.; Ferraudi, G.; Schmatz, K. *Inorg. Chem.* **1982**, 21, 2961.
- (21) Green, J. M.; Faulkner, L. R. *J. Am. Chem. Soc.* **1983**, 105, 2950.
- (22) Ohtani, H.; Kobayashi, T.; Ohno, T.; Kato, S.; Tanno, T.; Yamada, A. *J. Phys. Chem.* **1984**, 88, 4431.
- (23) Ough, E.; Gasyna, Z.; Stillman, M. *J. Inorg. Chem.* **1991**, 30, 2301.
- (24) Wynne, K. *J. Inorg. Chem.* **1984**, 23, 4658.
- (25) Guay, D.; Veilleux, G.; Saint-Jacques, R. G.; Côté, R.; Dodelet, J. P. *J. Mater. Res.* **1989**, 4, 651.
- (26) Nebesny, K. W.; Collins, G. E.; Lee, P. A.; Chau, L.-K.; Danziger, J.; Osburn, E.; Armstrong, N. R. *Chem. Mater.* **1991**, 3, 833.
- (27) Yanagi, H.; Douko, S.; Ueda, Y.; Ashida, M.; Wöhrle, D. *J. Phys. Chem.* **1992**, 96, 1366.
- (28) Chau, L.-K.; England, C. D.; Chen, S.; Armstrong, N. R. *J. Phys. Chem.* **1993**, 97, 2699.
- (29) Aroca, R.; Jennings, C.; Loutfy, R. O.; Hor, A.-M. *Spectrochim. Acta* **1987**, 43A, 725.
- (30) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, 112, 5525.
- (31) Adam, D.; Schuhmacher, P.; Slimmerer, J.; Häussling, I.; Slemensmeyer, K.; Etzbach, K. H.; Ringsdorf, H.; Haarer, D. *Nature* **1994**, 371, 141.
- (32) Karasek, F. W.; Decius, J. C. *J. Am. Chem. Soc.* **1952**, 74, 4716.
- (33) Abkowitz, M. A.; Bässler, H.; Stolka, M. *Phil. Mag. B* **1991**, 63, 201.
- (34) Abkowitz, M. A. *Phil. Mag. B* **1992**, 65, 817.
- (35) Gartstein, Yu. N.; Conwell, E. M. *Chem. Phys. Lett.* **1995**, 245, 351.
- (36) Enokida, T.; Hirohashi, R.; Nakamura, T. *J. Imaging Sci.* **1990**, 34, 234.
- (37) Tanako, S.; Mimura, Y.; Matsui, N.; Utsugi, K.; Gotsh, T.; Tani, C.; Tateishi, K.; Ohde, N. *J. Imaging Technol.* **1991**, 17, 46.
- (38) Bluhm, T.; Mayo, J.; Hamer, G.; Martin, T. *Proc. SPIE-Int. Soc. Opt. Eng. (Color Hard Copy Graphic Arts)* **1992**, 1670, 160.
- (39) Popovic, Z. D.; Hor, A. M. *Mol. Cryst. Liq. Cryst.* **1993**, 228, 75.
- (40) Saito, T.; Sisk, W.; Kobayashi, T.; Suzuki, S.; Iwayanagi, T. *J. Phys. Chem.* **1993**, 97, 8026.
- (41) Ghosez, Ph.; Côté, R.; Gastonguay, L.; Veilleux, G.; Denes, G.; Dodelet, J. P. *Chem. Mater.* **1993**, 5, 1581.