

THERMALLY STIMULATED SURFACE CURRENTS IN CH₃OH CRYOCONDENSATES NEAR THE POLYMORPHIC PHASE TRANSFORMATION

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Thermally stimulated surface currents (TSSCs) were measured in thin methanol cryocondensates after deposition of the layer onto a substrate at a temperature of 80 K from a molecular beam followed by heating at a constant rate. It was found that the TSSC curves exhibit some local maxima. One of these peaks was found near $T = 158$ K, *i.e.* in the temperature range where solid methanol undergoes a polymorphic phase transformation. The current–voltage characteristics obtained for these layers suggest fundamental changes in the electrical properties of the condensate surface that take place near this transformation ($\alpha \rightarrow \beta$). The current–voltage curve obtained at $T = 158$ K for the solidified methanol layer studied shows a similar shape to that of the current–voltage curves observed in dielectric materials within the space-charge-limited current range.

1. INTRODUCTION

Studies of the electret effect that appears in polar molecule cryocondensates during the condensation of molecular beams, performed in the last decade, suggest that the observed surface charges are mainly generated by a polar molecule polarization phenomenon^{1–5}. However, some of our recent observations⁶ have shown that some phase transformations occurring in the polar molecule condensates (*e.g.* of a structural type) may affect the value and sign of the surface charge of the condensate layer.

It has been suggested⁶ that some processes connected with the diffusion of free charge carriers inside the condensate, particularly in the neighbourhood of the structural phase transitions, may influence markedly the observed electret effect in these media.

The negative surface potential observed on methanol cryocondensates^{3,5} near the temperature $T = 158$ K corresponded to a structural phase transformation in the large methanol crystals^{7,8}. Hence it was interesting to see what kind of influence this transformation has on the electrical properties of the methanol condensate layer. The second interesting question was: Is the negative surface potential created by free charge carriers which are generated at this phase transformation or by the polarized molecular dipoles? Besides these basic questions, important for studies of

the electret effect, information concerning the electrical properties of thin films of the condensed gases and vapours is of considerable interest for low temperature electrical insulation.

2. EXPERIMENTAL DETAILS

Thermally stimulated surface current (TSSC) measurements were used in this research because of their great sensitivity and convenience⁹. The methanol layers studied were obtained during a process of methanol vapour condensation onto a substrate at 80 K in a vacuum of the order of 5×10^{-6} Torr. The process of condensation took place onto the surface of a measurement cell coupled to a heat exchanger. The system used allowed us to obtain the temperature of the measurement cell surface within the range 80–300 K. The temperature of the measurement cell was measured using a copper resistance thermometer or a precision copper–constantan thermocouple. The measurement cell consisted of a copper square plate (40 mm \times 40 mm) covered with a thin high resistivity dielectric layer of thickness 0.2 mm ($R_s > 10^{13}$ Ω cm at 300 K). Double comb-shaped (silver) electrodes were deposited onto this dielectric substrate. The mean separation between the electrodes was 0.5 mm. Except for the surface of the measurement cell the whole heat exchanger was shielded with a thermal screen at 300 K. This ensured vapour condensation onto the surface of the measurement cell only. The thickness of the methanol condensate layers varied from 5 to 50 μ m. The TSSC was measured using a vibrating reed electrometer. The heating rate used in all the experiments was constant at $dT/dt = 0.05$ K s⁻¹.

3. RESULTS AND DISCUSSION

The TSSC in the measurement cell when covered with the methanol cryocondensate layer was studied as a function of several parameters: (a) the measurement cell temperature T ; (b) the thickness d of the methanol layer; (c) the voltage U_p polarizing the electrodes of the measurement cell when the cell was covered with a condensed methanol layer. The characteristic current–voltage ($J-U_p$) curves were measured in separate experiments for temperatures near the phase transformation in solid methanol: $T_f = 157.8$ K⁷.

In all experiments the condensate layer was held in dynamic equilibrium with its saturated vapour. Therefore the thickness of the deposited condensate layer was approximately constant.

The TSSC curves presented in Fig. 1 show the dependence of the measured current in the measurement cell for layers of various thicknesses as a function of reciprocal temperature. The applied polarizing voltage U_p was 150 V. As is seen, the TSSC below $T = 175$ K, *i.e.* the melting temperature of solid methanol, is practically independent of the condensate layer thickness. The small scatter of the experimental points for the various thicknesses does not exceed the maximal experimental temperature error (± 3 K). A dependence of the TSSC on the thickness of the deposited layer appeared above 175 K and was linear (Fig. 1(b)). It follows that the TSSC measurements were associated with the electrical properties of the thin “subsurface” region of the methanol condensate layers.

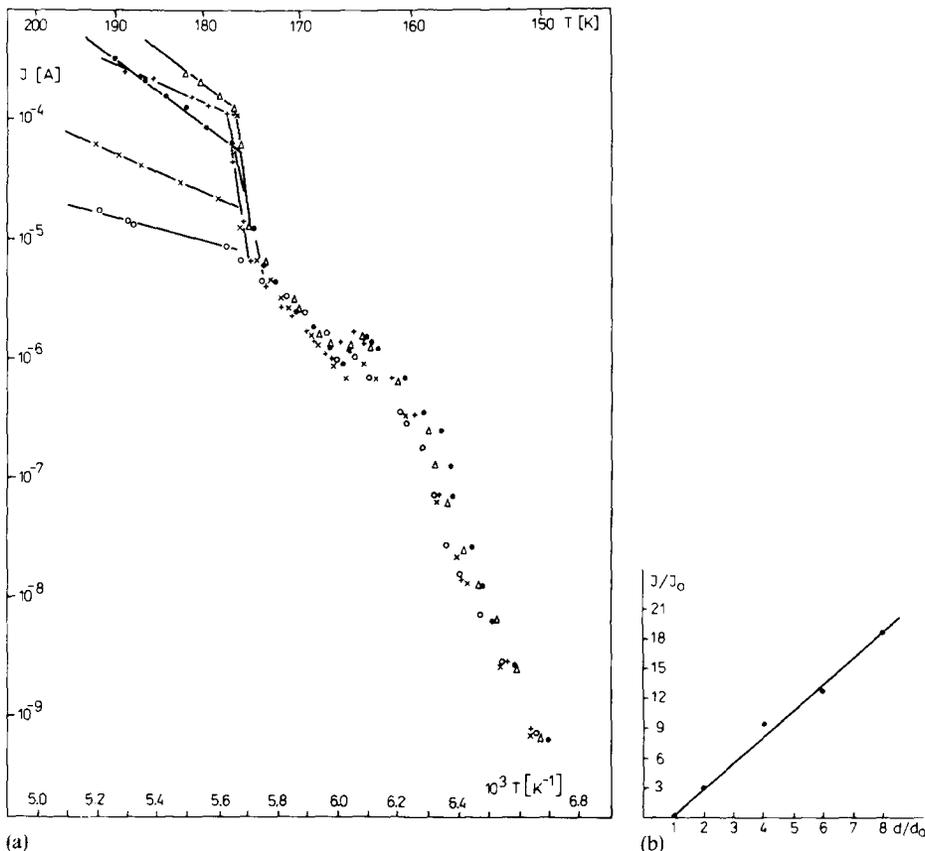


Fig. 1. (a) Thermocurrent plotted against reciprocal temperature for various thicknesses of the deposited methanol layers ($T_m \approx 175$ K): \circ , $5 \mu m$; \times , $10 \mu m$; \bullet , $20 \mu m$; $+$, $30 \mu m$; Δ , $40 \mu m$. (b) The reduced values of the measured thermocurrent as a function of the relative thickness of the deposited layer above the melting point temperature ($T = 180$ K).

The TSSC values obtained for the condensates, at various polarizing voltages, are presented in Fig. 2 plotted against the temperature of the measurement cell. As is seen, the dependence of the TSSC on the measurement cell temperature strongly depends on the polarizing voltage U_p . For small values of U_p (0.5–1 V) only one peak in the TSSC appears near the temperature 158 K, i.e. near the $\alpha \rightarrow \beta$ transition temperature. According to TSSC theory (see for example ref. 10), the thermally stimulated current peak appearing at a given temperature T_m is due to the ionization of some occupied trapping levels with energy E_t , given by the expressions $E_t \approx 23k_B T_m$ or

$$E_t = \frac{1.51k_B T_m T_{1/2}}{T_m - T_{1/2}}$$

where T_m is the temperature at which the respective maximum peak occurs, $T_{1/2}$ is the temperature at which the half-maximum peak height occurs and k_B is Boltzmann's constant. Therefore the trapping level corresponding to the peak maximum at 158 K is $E_t = 0.32$ eV.

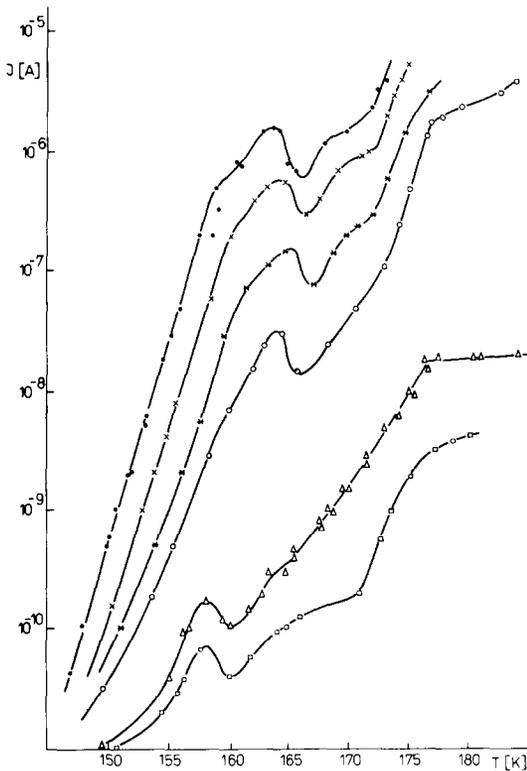


Fig. 2. TSSC curves registered for the methanol condensates at various polarizing voltages U_p : \square , 0.5 V; Δ , 1 V; \circ , 10 V; $*$, 50 V; \times , 100 V; \bullet , 300 V.

The initial parts of the TSSC curves for a low polarizing voltage were found to be superlinear but slowly became linear as the polarizing voltage was increased. This suggests that the recombination processes are dominated by effects other than the ionization of occupied trapping levels. Simultaneously, for $U_p = 300$ V, in addition to the peak at 158 K (weakly discerned in this curve) some further weak TSSC local maxima occur at the temperatures $T_1 = 163$ K and $T_2 = 168$ K. The slope of the initial part of the TSSC curves increases systematically with the polarizing voltage.

As is known¹¹, thin films of condensed gases and vapours when obtained at low temperatures show an amorphous or semiglassy texture. During the heating process some slow recrystallization processes take place inside the condensed layer, leading to the growth of microcrystallites. The size and nature of the structure of these microcrystallites depend on the temperature of the layer as well as on the heating rate. A number of such structural transformations have been observed in H_2O , CO_2 and similar substances (see for example refs. 12–15). The observed TSSC peaks may be connected therefore with these recrystallization processes and/or the liberation of some degrees of freedom of the molecules. However, processes of another nature also seem probable.

The appearance of additional TSSC peaks, which are absent in TSSC curves obtained for low polarizing voltages, may be associated with the injection of charge

carriers into the condensate layer from the electrodes. These charge carriers may be partly trapped in deep energy levels localized at the condensate surface itself. The remaining injected charge carriers are mobile in the conduction band, affecting the conductivity of the layer. These effects would lead to an increase in the TSSC as well as to the additional TSSC maxima in the higher temperature range. The deep trapping levels should be situated near the condensate free surface and may be created by structural surface defects and/or by adsorbed atoms or molecules.

The appearance of a TSSC peak near a temperature of 158 K on heating of the layer and the fact that the measured current flowed at the surface of the condensate suggest the existence of charge carriers with a greater concentration in the subsurface region of the layer. This phenomenon affected markedly the $J-U_p$ characteristics for the measurement cell covered with the condensed methanol layer near this temperature. $J-U_p$ curves are shown in Figs. 3 and 4 for various temperature ranges ($T < T_i$ and $T > T_i$) and for the temperature $T = 158$ K which is very close to the temperature T_i of the $\alpha \rightarrow \beta$ transformation. As is seen, the shape of the $J-U_p$ curves changes significantly at the temperature where the $\alpha \rightarrow \beta$ transition takes place. The $J-U_p$ curve obtained at $T = 158$ K for low polarizing voltages satisfies Ohm's law: $J \sim U_p$. At higher voltages U_p there is a rapid increase in the slope dJ/dU_p , subsequently going over to Childs' law; $J \sim U_p^2$ may be observed near $U_p = 300$ V.

This type of $J-U_p$ characteristic is usually observed in a dielectric material and is characteristic of so-called space-charge-limited currents (SCLCs)¹⁶. For dielectric materials the part of the $J-U_p$ curve with the greatest slope is connected with the emptying of charge carriers from the trapping levels by the applied electric field. Knowledge of the magnitude of the voltage at which this process occurs allows us to estimate the number N_t of trapping levels at the energy depth E_t . Applying the SCLC theory for dielectrics to our case we estimate that to a first approximation N_t is

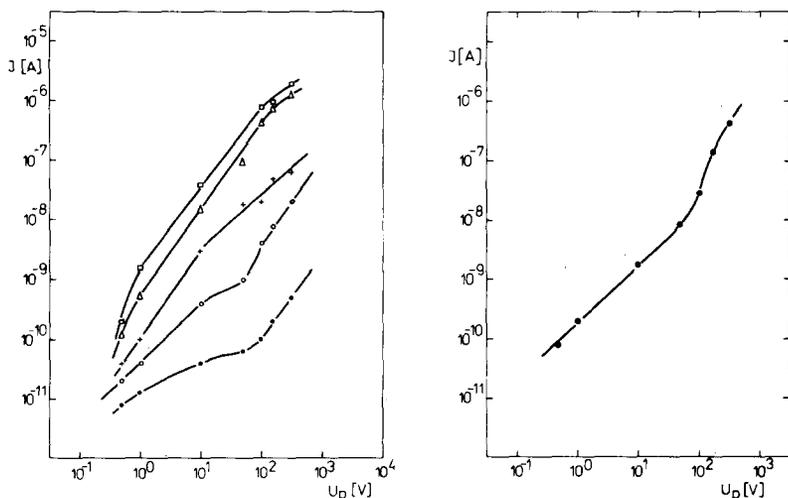


Fig. 3. $J-U_p$ curves obtained for the methanol condensates around the $\alpha \rightarrow \beta$ transition temperature: ●, 150 K; ○, 155 K; +, 160 K; △, 165 K; □, 170 K.

Fig. 4. $J-U_p$ curve obtained for the methanol condensate layer at $T = 158$ K.

approximately 10^{14} cm^{-3} . The distribution in energy of the trapping levels as calculated on the basis of the shape of the $J-U_p$ curve suggests a gaussian-type distribution with the lowest edge at approximately 0.5 eV below the bottom of the conductivity band.

The results presented above suggest that in the vicinity of 158 K an electrical space charge can occur. Assuming that this space charge is localized in a subsurface layer of the methanol condensate of thickness of the order of 10^{-6} cm we obtain the active number of trapping levels per unit area of the "physical" condensate surface: $N_{1s} \approx 10^8 \text{ cm}^{-2}$. Taking into account that most of these subsurface active trapping levels are occupied at the phase transformation we calculated the density σ of the subsurface charge. The estimated value of σ is of the order of $10^{-11} \text{ C cm}^{-2}$. This is in good agreement with the earlier value estimated for methanol condensates at 158 K³. These considerations are probably valid in the temperature region close to the $\alpha \rightarrow \beta$ transformation temperature only. Outside this temperature range the carrier injection processes, mentioned earlier, may affect the observed effects to a large degree.

The appearance of space charge at the condensate surface suggests that other electrical properties of the methanol condensate layers should also change in this temperature range. The measurement surface cell used for the TSSC study may be treated as an electrical capacitor¹⁷ (see also ref. 18 for the preparation of the cells for surface conductivity studies of organic films). The capacitance of this capacitor depends directly on the dielectric permittivity of the insulating substrate (a 0.2 mm glass plate stuck to the copper base plate) and on that of the deposited layer. This capacitance also depends linearly on the deposited layer thickness. It was checked that the change in capacitance of the "empty" (without any condensed layer) capacitor in the temperature range of interest may be neglected. In all capacitance measurements the copper base plate (an element of the heat exchanger) was held at earth potential. Therefore measurements of the capacitance of the capacitor covered with the methanol layer give at least qualitative information concerning the temperature dependence of the permittivity $\epsilon = \epsilon(T)$ of the condensate for the frequency $\omega = 10^4 \text{ rad s}^{-1}$. The experimental results obtained using a semi-automatic precision bridge for a layer thickness of about $50 \mu\text{m}$ are presented in Fig. 5.

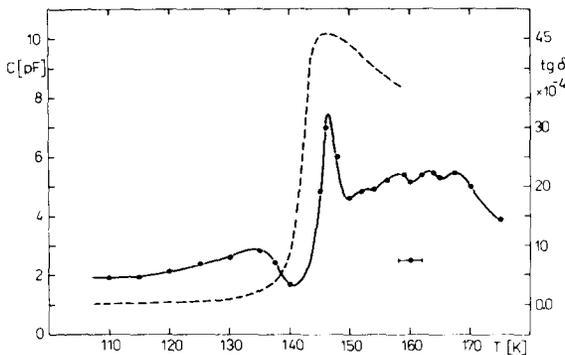


Fig. 5. The temperature dependence of the capacitance $C = C(T)$ of the measurement cell covered with the $50 \mu\text{m}$ methanol layer: ---, the observed loss tangent $\tan \delta$.

Significant changes in the measured capacitance $C(T)$ appear within the temperature range 135–170 K. A series of local maxima appear at $T_1 = 146$ K, $T_2 = 153$ K, $T_3 = 158$ K, $T_4 = 163$ K and $T_5 = 168$ K respectively. Some of these “peaks” coincide with the TSSC maxima presented in Fig. 2 for higher polarizing voltages U_p . In Fig. 5 the variation in the loss tangent $\tan \delta$ with temperature is also shown. $\tan \delta$ attains large values rapidly but the shape of the $\tan \delta(T)$ curve is hardly reproducible. These observations also suggest a substantial change in the electrical properties of the layer within the temperature range studied.

It is also worth while mentioning that another structural phase transformation in the methanol layer should occur in the temperature range 80–100 K as can be concluded from the measurements shown in Fig. 6. In the same temperature range a high “peak” can be observed in the electrical charge appearing during condensation at the free surface of a freshly condensed layer⁵. It should also be mentioned that in the temperature range 80–100 K no change can be found in $\tan \delta$ (Fig. 6).

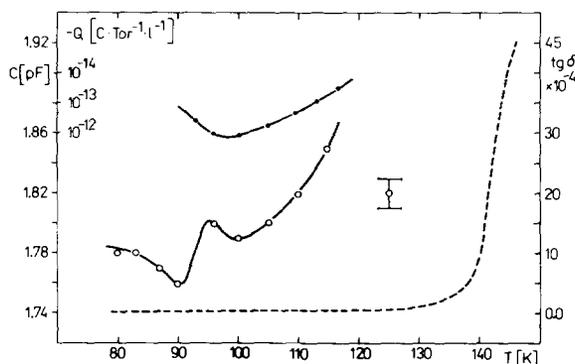


Fig. 6. The measurement cell capacitance (○) and loss tangent (---) obtained for a 50 μm layer within the temperature range 80–120 K: — —, the observed temperature dependence in this temperature range of the electrical charge on the free surface of the methanol condensate.

All these facts seem to indicate that within the 80–100 K temperature region we have to deal with an electret effect due to a spontaneous low temperature molecular polarization process. Therefore no free charge carriers should be expected, in contrast with the case of the $\alpha \rightarrow \beta$ phase transformation in the vicinity of 158 K.

4. FINAL REMARKS

The effects observed at about 135–170 K are indubitably connected with the structural phase transformation $\alpha \rightarrow \beta$ in CH₃OH. These effects appearing within a relatively large temperature region are difficult to attribute to the structural phase transformation at 157.8 K only. Such behaviour of the condensate may be caused by the occurrence of some other non-stable modifications co-existing with the α or β phase of the solid methanol and appearing in the temperature range 135–170 K. As is known, the molecular solids show plenty of phase transformations in which the increase in entropy due to rotation is subtly balanced against the loss of binding energy due to loss of orientation order¹¹.

The process of injection of free charge carriers into the studied layer from the electrodes seems to have an important effect on the observations, especially outside the $\alpha \rightarrow \beta$ transformation temperature region, and for the high polarizing voltages applied.

The occurrence of space charge in the subsurface layer close to 157.8 K has great significance for the interpretation of the surface charge generation process in polar molecule condensates. The results suggest that the surface charge appearing at 158 K at the free surface of the methanol condensate⁵ may be created, at least partly, by space charge comprising free charge carriers produced by the phase transition. A negative surface potential observed at this temperature⁵ suggests negatively charged carriers. Thus the simple model of the polarized condensate discussed in refs. 1 and 3–5 is probably not valid for the 135–170 K region discussed here in the case of methanol cryocondensed layers, in contrast with the effects observed in the same methanol layers below 135 K.

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