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ELECTRICAL CONDUCTIVITY OF PLASTIC CRYSTALS: dl-CAMPHORIC ANHYDRIDE, dl-2,3-CAMPHANEDIONE AND dl-CAMPHOR OXIME*

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Electric conductivity measurements of camphoric anhydride, camphanedione and camphor oxime single crystals and polycrystalline samples have been performed in the temperature region referred to as the brittle-to plastic phase transition. Phase transition temperatures indicated by the electrical conductivity jump agree with the calorimetrically obtained results of 408.5 K, 320 K and 385.5 K for the above compounds, respectively. Electrical conductivity of polycrystalline samples strongly depends on recrystallization occurring at high temperatures and on macrostructural effects which accompany the phase transition. The ionic model of electrical conductivity has been put forth to explain the observed properties of the investigated samples.

1. Introduction

The plastic crystal is the well known solid phase, common among molecular crystals build from globular molecules [1–3]. Macroscopically they differ from "normal" or "brittle" crystals by their low value of entropy of fusion [2], microscopically — by the rotational motion of molecules as revealed by dielectric [4–6] and NMR-spectroscopy [1, 7, 8]. Both NMR-spectroscopy [9, 10] and the radiotracer method [11] confirm the primary role of the lattice point defects in mass transport in the plastic phase.

Electrical conductivity was investigated in only a few plastic crystals those being d-camphor [12], dl-camphanedione [13], d-camphoric anhydride [14] and pivalic acid [15]. For d-camphor and dl-camphanedione similar changes in conductivity and thermal activation energy of the conductivity at the transition temperature were reported, the latter being lower in the plastic phase than in the brittle one. On the contrary, Yager and Morgan did not find any effect of phase transition on dc-conductivity of the camphoric anhydride [14].

The mechanism of conduction in plastic crystals is not known so far. In view of the

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* Dedicated to Professor Kazimierz Gumiński on the occasion of his 70-th birthday.

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rotational motion of molecules, the tunneling mechanism elaborated by Gutmann [16] or proton conductivity model proposed for imidazole [17, 18] might be operating here. On the other hand, enhanced diffusional motion is compatible with ionic conduction similar to that observed in insulating liquids.

The scope of this work was to try the question of the mechanism of conduction in plastic crystals by dc-conductivity measurements on single crystals and polycrystalline samples of camphoric anhydride, camphanedione and camphor oxime in the plastic phase, and in the brittle one, especially within the phase transition region.

2. *Experimental*

Racemic camphoric anhydride, 2,3-camphanedione and camphoric oxime have been synthesized starting from dl-camphor. Products were repeatedly purified by sublimation followed by crystallization from methanol. Gas chromatography tests of the purest fractions of camphoric anhydride and 2,3-camphanedione disclosed less than 0.2 wt. pct contaminants. They were probably the residual slovents used in the recrystallization procedure. dl-Camphoric oxime contained neither camphor nor solvent.

Single crystals of the brittle phase of camphoric anhydride were grown by sublimation in glass ampoules in a furnace, similar to the one designed by Radomska et al. [19]. Single crystals of camphanedione and camphor oxime were grown by slow evaporation of the solvent from benzene solutions at ambient temperature.

The best solution-grown crystals of the platelet shape (dimensions of $2\times2\times0.5$ mm) were tested in a polarising microscope and used in measurements. Suitable crystals of camphoric anhydride were cleaved from boules grown in the sublimation apparatus. Electrodes and the guard ring have been painted with silver paste.

Polycrystalline samples have been prepared by cooling the material melted between the platinum electrodes or by pressing the ground powder in a matrix under a pressure of 300 MPa.

Electrical measurements have been carried out in a nitrogen atmosphere. The temperature of the specimen was changed from ambient up to 500 K at a nearly constant rate of about 1.5 K min^{-1}. Temperature has been measured with Cu-constantan thermocouple mounted nearby the sample. Current was measured with VAJ-51 vibrating-reed electrometer, at a constant voltage, in the increasing and decreasing regime.

Routine calorimetric experiments were performed using a Perkin Elmer DSC-1B differential scanning calorimeter (d. s. c). Its temperature scale has been calibrated on the melting points of several organic compounds of high purity, the errors being less than 0.5 K, over the range of $300\div500$ K.

3. *Results and discussion*

3.1. Calorimetric observations

D. s. c. curves of the compounds investigated are shown in Fig. 1. Vertical arrows indicate the temperatures of polymorphic transitions and melting. Corresponding values are collected and compared to literature data in Table I. In the next columns of Table I the values of molar entropy and molar heat of transition as calculated from the area of peaks are summarized together with appropriate literature data.

The temperature intervals of the phase existence detected in our experiments are in good agreement with the literature [1, 20].

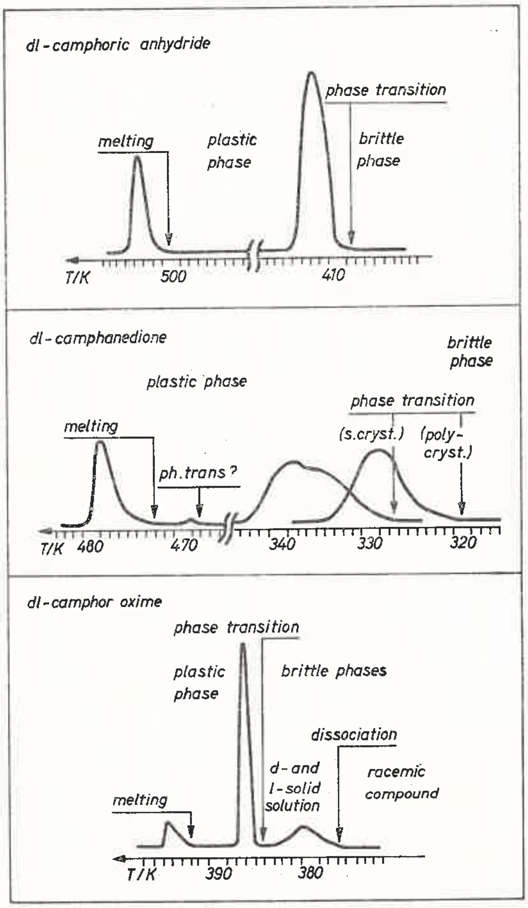

Fig. 1. D.s.c. curves for dl-camphoric anhydride, dl-2,3-camphanedione and dl-camphor oxime near phase transition regions

A small additional endothermic effect, suggesting phase transition near 468 K was observed in dl-2,3-camphanedione in each experiment. The problem, being beyond the scope of this work, has been not studied in detail.

3.2 Electrical conductivity of single crystals in the brittle phase

Electrical conductivity of single crystals of the three compounds in the brittle phase was lower than we could measure. Current flowing through a bulk single crystal equipped with a guard ring electrode was lower than 10^{-14}A even at the field strength of 10^5V m^{-1}, up to the phase transition temperature. At this temperature current increased suddenly

TABLE I

Phase transition parameters taken from d.s.c. measurements

Phase transition	Transition temperature [K]	$\Delta H_{\text{ph.tr.}}$ [kJ mole^{-1}]	$\Delta S_{\text{ph.tr.}}$ [J K^{-1} mole^{-1}]	References
	dl-camphoric anhydride			
brittle to plastic phase	408			[1]
	408.5	21.2	51.8	this work
plastic phase to liquid	495		16.8	[1]
	500	7.52	15.0	this work
	dl-2,3-camphanedione			
brittle to plastic phase II	318÷328			[1]
	327^{a}			this work
	320^{b}	13.2	41.4	this work
plastic II to plastic I?	468	0.27	0.58	this work
plastic I to liquid	472		14.3	[23]
	473	6.03	12.8	this work
	dl-camphor oxime			
decomposition of racemic solid compound, brittle phases	376.5			[24]
	377			this work
brittle to plastic phase	382.5		18.2	[24]
	383			[20]
	385.5	4.68	12.1	this work
plastic phase to liquid	392			[24]
	393	2.28	5.8	this work

[a] single crystal, [b] polycrystalline sample.

by several orders of magnitude as is shown in Figs 2a, 3a, 3b. There is perfect agreement between the temperature, at which the abrupt rise in the conductivity was observed and those estimated in d. s. c. measurements, and listed in Table I. The differences are less than 0.5 K.

The phase transition inevitably transformed single crystalline specimens into polycrystalline ones. Their polygonal structure was confirmed by X-ray Laue patterns obtained when a single crystal of the brittle phase was heated above the transition temperature.

The strong increase in electrical conductivity in the transition region, observed when brittle crystals transformed to the polycrystalline plastic phase, might be due either to

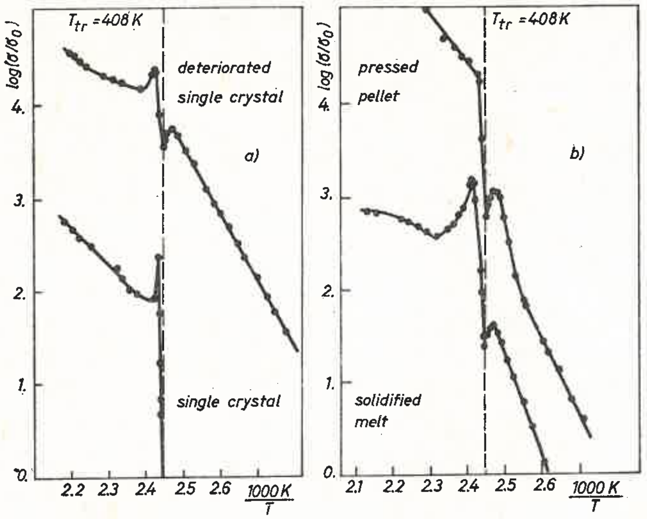

Fig. 2. Electrical conductivity of dl-camphoric anhydride samples at the phase transition region near 408 K. Transition temperature of 408 K marked with dashed lines was detected by electrical measurements. a — The first heating run of the single crystal (deteriorated in the plastic phase) and the second heating run of the same sample, b — samples obtained from the melt and pressed pellet

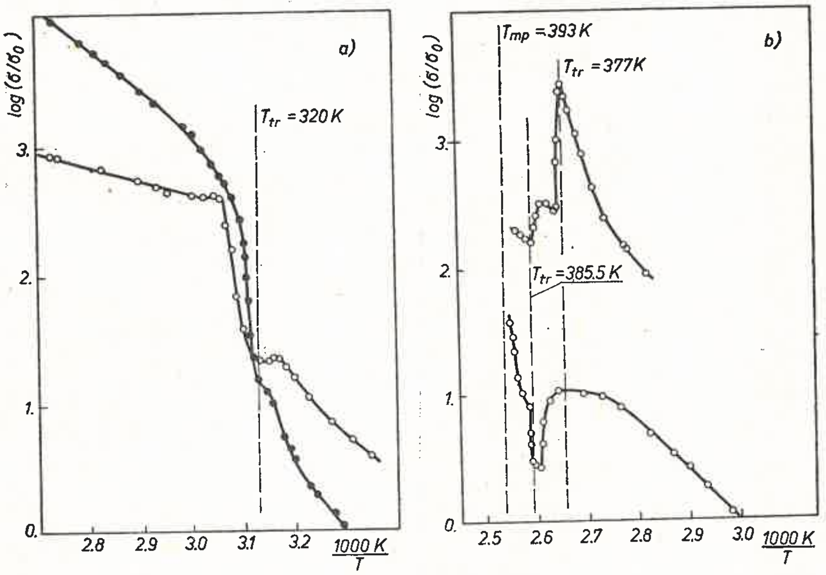

Fig. 3. a — Electrical conductivity of dl-2,3-camphanedione at phase transition region 320÷328 K. Transition temperatures are marked according to electrical measurements. The first heating run of a single crystal — open circles, cooling run — crosses, the second heating run of polycrystalline sample — full points. The value of the constant σ_0 is the same for all specimens. b — Electrical conductivity of dl-camphor oxime at phase transition regions 377 and 384.5 K, the transition temperatures were detected by electrical measurements. The first heating run for a sample obtained from single crystal deteriorated during the first phase transition

intrinsic differences in electrical properties of the phases or/and to changes of macrostructural order in the sample. These two effects should be separated prior to any discussion of the influence of phase transformations on electrical conductivity.

Unfortunately, we did not succeed in growing single crystals of the high temperature plastic phase sufficiently large and free of macrostructural defects for use in conductivity measurements. Therefore we could not solve this problem directly by experiment.

3.3. Electrical conductivity response to phase transition of polycrystalline dl-camphoric anhydride

As is already stated, the curves shown in Figs. 2a, 3 represent the electrical conductivity of polycrystalline material formed by the deterioration of a single crystal. Results obtained in the first heating run for this reason differ significantly from those found in the next runs. Subsequent cooling or heating runs render polycrystalline material only.

In Fig. 2 the results obtained for the deteriorated single crystal of dl-camphoric anhydride (Fig. 2a) are compared with those found for the pressed pellet and specimen obtained from the melt (Fig. 2b). The curves have been arbitrarily shifted along the ordinate axis for clarity.

Qualitatively, changes in the conductivity at phase transition are similar with respect to the general shape for all types of polycrystalline samples. The electrical conductivity

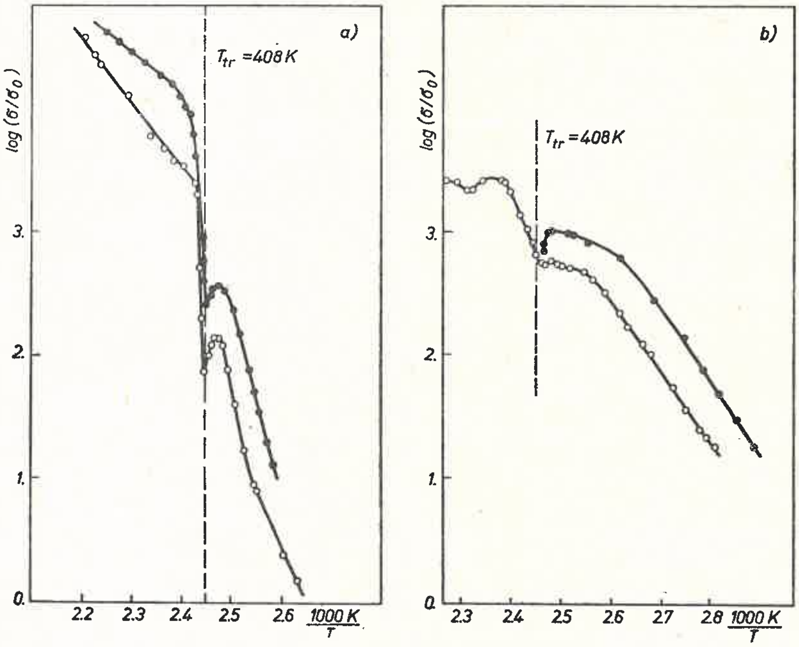

Fig. 4. a — Electrical conductivity of dl-camphoric anhydride measured in dc. (open circles) and ac. (full points) experiments. The values of the constant σ_0 are arbitrarily chosen for both cases. b — Recrystallization effect on electrical conductivity of dl-camphoric anhydride polycrystalline sample. Full points — the first heating run up to the vicinity of phase transition temperature of 408 K. Open circles — the second heating run

of the polycrystalline specimens goes over a local maximum just before the transition. Then it changes more or less sharply at the transition point. After that, the electrical conductivity of the sample passes another maximum and from this point the sample reveals the normal exponential dependence of conductivity on reciprocal temperature.

Some experiments using ac. techniques have been done to check the possible influence of persistent polarisation on conductivity measurements in the transition region. The results of two experiments (heating runs) performed on two pellets of dl-camphoric anhydride using dc. and ac. technique are shown in Fig. 4a. Square voltage pulses of polarisation alternating at frequency 0.2 Hz were used in the ac. experiment. There are no essential differences in the shape of the dc. and ac. curves, which supports the suggestion that anomalies observed in the transition region do not depend on the polarising mechanism.

Polycrystalline samples of dl-camphoric anhydride in the plastic phase when cooled below the transition temperature, change their electrical conductivity due to transformation to the brittle phase. The change although abrupt occurs at a random temperature, everytime significantly below $T_{tr} = 408$ K.

The interpretation of electrical conductivity response to transition in cooling conditions is complicated and hardly possible. Similarly, post-transition phenomena occurring in heating runs are difficult to discuss for they are preceded by a phase transition and are beyond external control. Thus, we are dealing here with the pre-transition phenomena only, which occur within the range of existence of a particular phase.

Neither d. s. c. experiments (see Fig. 1) nor dielectric studies by Yager and Morgan [14] on dl-camphoric anhydride reveal any pre-transition phenomena below 408.5 K. Nevertheless, the electrical conductivity changes its value before the transformation has begun. This effect, as well as the large difference in conductivity of the single crystals as compared to polycrystalline samples of the brittle phase, lead to the following conclusion: the electrical conductivity of the polycrystalline sample depends on its macrostructural conditions and therefore a crystallization process occuring in polycrystalline material demonstrates itself in the conductivity.

Recrystallization of grains is easy to observe in the pretransition region by an X-ray diffraction experiment. A polycrystalline sample held at a constant temperature of 400 K for one hour and a freshly prepared one exhibit quite different Laue patterns. That of the former shows a smaller number of the spots than that of the latter.

The conductivity related to the grain structure of the sample should irreversibly change within the range of the existence of the phase, correlated to changes in crystallinity.

In Fig. 4b the results of an annealing experiment performed on polycrystalline dl-camphoric anhydride are shown. The pellet was heated up just below the phase transformation temperature and held at that temperature for one hour to allow recrystallization. Then the sample was cooled down and heated again until the transformation to the new phase began. The decrease in conductivity in the course of annealing as well as the diminution of the pre-transition maximum of conductivity in the next heating run, corroborate the assumption that the changes in grain structure are responsible for the pre-transition phenomena observed in our experiments.

Substracting the recrystallization effect from the overall change in conductivity observed at phase transition one can find conductivity of the polycrystalline plastic phase to be higher than that of the polycrystalline brittle phase.

In a heating run within the range of the existence of a given phase, electrical conductivity changes according to the exponential relationship of the thermally activated process and additionally due to recrystallization. At high temperatures, when the latter process is quick enough, the conductivity is strongly modified by recrystallization, thus a straight line plot $\log \sigma$ vs. $1/T$ is never observed. Moreover, the thermal activation energy, E, calculated from the formal equation $\sigma = \sigma_0 \exp(-E/kT)$ depends on the thermal history of the specimen prior to measurement. The formal "thermal activation energy", E, lacks physical meaning and only roughly gives information about real activation energy of the brittle and plastic phase. Nevertheless, for all specimens of dl-camphoric anhydride we have experimented with, formal "activation energy" for the plastic phase was smaller than that for the brittle phase and we do belive this result is representative of the real situation.

3.4. Electrical conductivity of polycrystalline dl-2,3-camphanedione and dl-camphor oxime in the brittle and plastic phase

Measurements of the electrical conductivity of dl-2,3-camphanedione by the same technique as reported for dl-camphoric anhydride show that polycrystalline samples of both compounds behave similarly in heating runs regarding the response of conductivity to phase transformation.

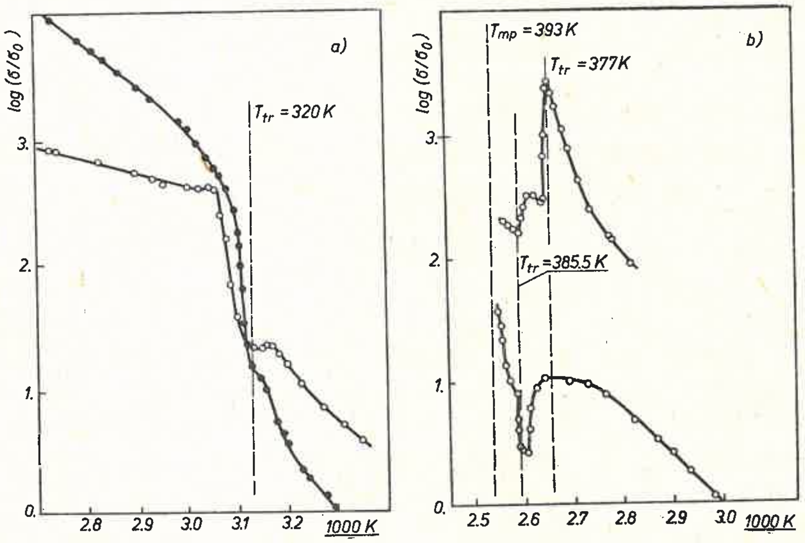

Fig. 5. a — Electrical conductivity of dl-2,3-camphanedione at phase transition region. Phase transition temperature of 320 K was detected by d.s.c. Heating runs for a pressed pellet (open circles) and a specimen obtained from the melt (full points). b — Electrical conductivity of dl-camphor oxime at phase transition regions. Phase transition temperatures of 377 K and 385.5 K and melting point of 393 K were taken from d.s.c. Heating run for polycrystalline sample obtained from the melt (lower line) and pressed pellet (upper line). The values of σ_0 constant are different

In Figs 3a and 5a the results of the measurements performed on polycrystalline samples obtained from a single crystal and from the melt as well as from a pressed pellet of dl-camphanedione are shown. Curves in Fig. 5a are arbitrarily shifted along the ordinate axis.

Fig. 5a when compared to Fig. 2 reveals similarities in electrical behaviour of camphanedione and camphoric anhydride in phase transition region. Similarly to camphoric anhydride, polycrystalline camphanedione changes its electrical conductivity due to recrystallization. Conductivity of the plastic phase corrected for the recrystallization effect is always higher than that of the brittle phase. The reverse is found for "thermal activation energies" of conductivity.

The results for dl-camphoric oxime are more difficult to discuss, but may be also explained using the model elaborated for camphoric anhydride. The conductivity of polycrystalline samples of dl-camphoric oxime measured in the heating run is shown in Figs 3b and 5b. Due to the narrowness of the existence interval of the plastic phase, the rate of recrystallization is quite high even at the phase transition temperature. Depending on the crystallinity of the original brittle phase, one observes a different electrical behaviour in the vicinity of phase transition points at 377 K and near 385 K.

Conductivity of the pressed pellet measured on heating diminishes during phase transitions (see Fig. 5b) whereas that of the deteriorated single crystal increases (see Fig. 3b). Intermediate behaviour is observed for polycrystalline specimens obtained from the melt, which reflects the intermediate degree of crystallinity in these samples. Above 377 K the brittle phase of solid solution of stereoisomers [20] recrystallizes and conductivity decreases on heating up to the vicinity of the brittle to plastic transition (385.5 K) and then starts to increase.

4. *Conclusions*

The characteristic features of electrical conductivity of plastic crystals studied in this paper might be summarised as follows:

1. Electrical resistivity of sample both in the brittle and in the plastic phase strongly depends on the degree of crystallinity, for single crystals of the brittle phase being higher than 10^{16} ohm.
2. Phase transition from brittle to plastic phase is accompanied by pre- and post-transition phenomena manifesting themselves by maxima on $\log \sigma$ vs. $1/T$ plot. These effects, kinetic in nature, are presumably due to a comparatively high rate of recrystallization in the vicinity of the phase transition point.
3. Resistivity and its apparent thermal activation energy are lower for the plastic phase than for the brittle one.
4. There are no significant differences in the behaviour of dl-camphoric anhydride, dl-2,3-camphanedione and dl-camphor oxime with respect to features stated under $1 \div 3$.

Seeking an explanation of these facts, one should discuss the mechanism of electrical conductivity in the materials. There is no experimental evidence for preclusion or to acceptance any of the mechanisms mentioned in the introduction. Moreover, there is no basis for determining whether the nature of charge carriers is electronic or ionic.

A lot of facts concerning the plastic crystals known from the literature allow us to suggest and to try a hypothesis which takes into account the ionic transport mechanism.

Already Yager and Morgan [14] have assumed ionic conductivity in liquid and solid camphoric anhydride. Williams, Cox and Thomas have stressed the significance of the high density of point defects in plastic crystals for their enhanced conductivity [13].

Sherwood et al. [11] have found that the self-diffusion coefficient for the plastic phase is several orders of magnitude greater and its thermal activation energy significantly lower than that for the brittle one. It is reasonable to expect the same to be true for the diffusion coefficients of intrinsic and extrinsic ions and according to the Einstein relation also for their mobilities.

Moreover, as the static electric permittivity of the plastic phase is considerably higher than that of the brittle one [14, 22], generation of ions in the plastic phase should be enhanced too. These facts are consistent with our results cited in point 3 above.

Diffusion in polycrystalline materials depends on grain boundary diffusion coefficient, which surpasses by several orders of magnitude that for bulk diffusion [11, 21]. One can expect that in single crystals where only the latter mechanism in operative, conductivity would be extremely low and in polycrystalline material recrystallization would result in a decrease in conductivity. Our results corroborate this picture as stated in points 1 and 2 so the ionic model of carrier transport in the compounds investigated seems to be realistic one.

It is impossible, however, to define the nature of ions which would be responsible for the observed conductivity. One has to stress that in spite of all our attempts, the materials used in our experiments were of low purity in terms of solid state physics. Plastic crystals of bornane derivatives are extremely resistant to purifying procedures and usually contain astonishingly high amounts of impurities [10], water and isomeric compounds being the most common ones. It is possible that extrinsic ions (protons or ionised impurity molecules) are responsible for the observed conductivity. This is, however, difficult to prove, because of the unavoidable thermal decomposition of molecules during prolonged experiments which would mask any electrolytic effects.

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