

Solid State Transitions in Alkali Alkanoates: Diffraction and Conductometric Measurements on Lithium, Sodium and Potassium Propanoates

A. Cingolani, G. Spinolo, and M. Sanesi

Centro di Studio per la Termodinamica ed Elettrochimica dei Sistemi Salini Fusi
e Solidi del C.N.R. c/o Istituto di Chimica Fisica e di Elettrochimica
dell'Università, Pavia, Italy

Z. Naturforsch. **34a**, 575–578 (1979); received March 26, 1979

Conductometric measurements on solid lithium, sodium and potassium propanoates and X-ray powder diffraction measurements on the sodium and potassium salts have been performed over temperature ranges including solid state transitions. The temperature dependence of the transport and lattice parameters of the different crystalline phases and the changes of the same parameters in correspondence with phase transitions have been put into evidence.

1. Introduction

The melting of the alkali salts of the alkane carboxylic acids is in several cases a stepwise process, involving intermediate stages between the true crystalline solid and the isotropic liquid; in particular the formation and properties of mesomorphic phases have been studied from several points of view and with different techniques (X-ray, dilatometry, electrical conductance, viscosity, etc.; see, e.g. [1], [2]).

Several crystalline forms are often encountered with these salts; for what concerns the structural features of the different polymorphs, a number of investigations on salts with long chain anions may be found in the literature [3]. In order to better understand the role played by the ionic portion of the molecule, the lower homologues ought to be considered preferably and, among these, the propanoates which have, unlike the acetates, possibilities of configurational motions that markedly affect the thermal behaviour.

It has been pointed out [4] that investigations concerning solid state transitions (sstr) are of remarkable interest for understanding the mechanism of entropy increase in this salt family. Such sstr's, however, are often characterized by very little structural changes (to which small heat effects correspond): in these cases investigations of equilibrium properties alone might not suffice and be paralleled by measurements of some transport property.

The present paper deals with diffraction and conductometric measurements on lithium, sodium and potassium propanoates (which have been proved not to exist as anisotropic liquids [5]), aiming at putting into evidence the changes of lattice and transport parameters connected to sstr's.

2. Experimental

The salts investigated were prepared and handled according to [5].

The lattice parameters were determined by polythermal X-ray powder diffraction, employing a Philips PW 1011 Diffractometer (with Cu fine focus tube, usually operating at 38 kV and 18 mA; proportional detector; ratemeter; timerscaler; and recorder) and a polythermal chamber built up in this Institute and described elsewhere [6].

Powder patterns were indexed following De Wolff's method [7]: the calculated densities were in accordance with the pycnometric ones ($d = 1.49 \pm 0.03$ and 1.45 ± 0.01 g cm⁻³ for the Na and K salt, respectively). The reliability index [8] of the unit cells was seldom between 15 and 25, but usually larger than the latter number. The lattice parameters were obtained by means of a computer program which minimizes the weighted sum of the squares of the differences between experimental and calculated Q values ($Q = 4 \sin^2 \theta / \lambda^2$).

The measurements of conductance, G , were carried out with a Wayne-Kerr Autobalance Precision Bridge mod. B 331 Mk II (frequency: 1592 Hz; conductance range: 10^{-10} – 10^{-2} S) on pellet-shaped cells (8 mm in diameter; 5–7 mm thick) obtained by pressing the salt powder between

Reprint requests to Prof. M. Sanesi, Istituto di Chimica Fisica e di Elettrochimica dell'Università, Viale Taramelli, 16, I-27100 Pavia (Italy).

0340-4811 / 79 / 0500-0575 \$ 01.00/0



Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

two silver powder layers. Details on the cells and on the cell-furnace assembly have been reported previously [9]. Heating was accomplished by means of an L & N temperature programmer and power unit. The outputs from the measuring thermocouple (type K) and from the bridge were fed to the same recorder to detect continuously (heating rate: $\sim 2 \text{ K min}^{-1}$) the temperature dependence of the solid phase conductance. As a rule, different experimental runs were carried out on four or more pellets for each salt.

Derivative plots ($d \log G/dT$ vs. T) were employed for a better characterization of the sstr regions, whereas a linearized least-squares analysis of the Arrhenius plots ($\log G$ vs. $1/T$) allowed to evaluate the activation energies, E_a , of the conductance process. To a first approximation the latter might be considered as equivalent to the activation energies for specific conductivity, E_κ *.

An approximate knowledge of the cell constants (from the geometrical dimensions of the pellets) allowed to obtain the order of magnitude of the specific conductivity, κ .

3. Results and Discussion

The sstr temperatures of the salts here concerned, as detected by differential scanning calorimetry (DSC) between 110 K and the melt region [5], were as follows:

Li propanoate ($T_F = 606.8 \text{ K}$): $T_A = 553 \pm 2 \text{ K}$,
 Na propanoate ($T_F = 562.4 \text{ K}$): $T_A = 494 \pm 1 \text{ K}$;
 $T_B = 470.2 \pm 0.6 \text{ K}$,
 K propanoate ($T_F = 638.3 \text{ K}$):
 $T_A = 352.5 \pm 0.6 \text{ K}$;
 $T_B = 258 \pm 2 \text{ K}$.

The several polymorphs of each salt are indicated hereafter as phase I, phase II, etc., starting from that stable at higher temperature.

The conductance measurements were carried out in the temperature ranges 480–540 for Li propanoate, 420–540 for Na propanoate and 320–630 K for K propanoate, the lowest limit being imposed by the instrumental sensitivity. It was not possible, therefore, to perform measurements on phase III of K propanoate, neither to detect for the same salt sstr A, in correspondence

* This can be inferred from the expansion coefficients of the solid salts, as deduced from the temperature dependence of the lattice parameters.

to which the change in the conductance values was below the experimental accuracy.

The derivative plots $d \log G/dT$ vs. T are shown in Figure 1: good agreement with the DSC sstr temperatures is apparent. The main results are summarized in Table 1, where the specific conductivity values of the phases in equilibrium at the

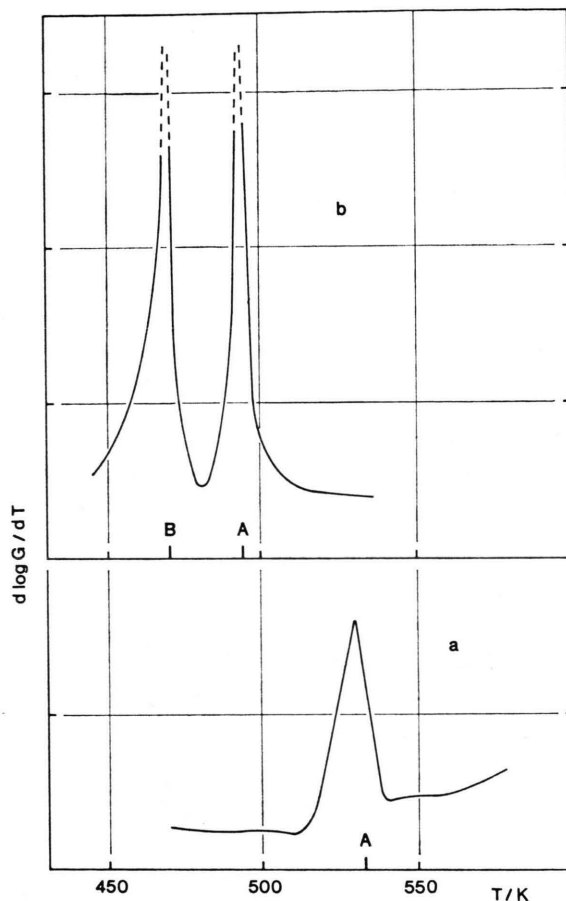


Fig. 1. Conductometric detection of the sstr temperatures in Li propanoate (a) and Na propanoate (b). The DSC values are indicated by vertical lines on the abscissa.

Table 1. Electrical conductance parameters for Li and Na propanoate solid phases.

Salt	Phase	Temperature range [K]	κ_{tr} S m^{-1}	E_κ kJ mol^{-1}
Li propanoate	I	530–580	$3.6 \cdot 10^{-6}$	149 ± 8
	II	480–530	$6.5 \cdot 10^{-7}$	61 ± 8
Na propanoate	I	494–540	$1.7 \cdot 10^{-3}$	118 ± 10
	II	470–494	$1.3 \cdot 10^{-4}$	123 ± 8

transition temperature, κ_{tr} , are reported along with the activation energies of the same phases. It was not possible to evaluate E_{κ} for phase III of Na propanoate and phase I of K propanoate, since $\log G$ is not a linear function of $1/T$ in these cases. For the latter phase the measured κ values ranged from $\sim 1.7 \cdot 10^{-8} \text{ S m}^{-1}$ at 373 K to $\sim 2 \cdot 10^{-5} \text{ S m}^{-1}$ at 573 K. The present E_{κ} value for phase I of Na propanoate is in satisfactory agreement with that reported by Duruz et al. [2] (112 kJ mol $^{-1}$) for a narrow temperature range (542–558 K) close to the melting point.

It is to be remarked that the activation energy in Li propanoate impressively increases in the transition from the lower to the higher temperature phase, whereas in the Na salt practically the same E_{κ} value is exhibited both by the I and II phase. The latter fact might be also related to the close similarity in the structure of these phases, as shown by the subsequent X-ray measurements.

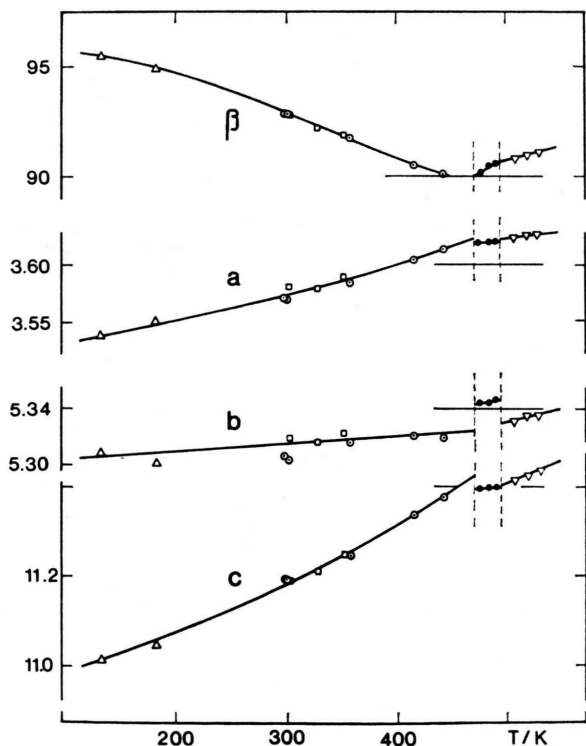


Fig. 2. Temperature dependence of the lattice parameters in phases I, II and III of Na propanoate (a, b and c in Å, β in degrees; different symbols refer to different investigated samples).

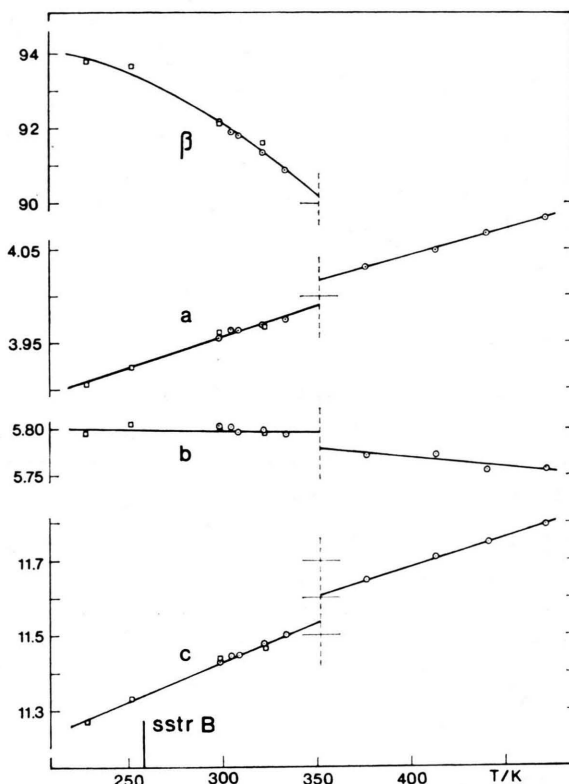


Fig. 3. Temperature dependence of the lattice parameters in phases I and II of K propanoate (a, b and c in Å, β in degrees; different symbols refer to different investigated samples). The points at temperatures below sstr B (indicated by a vertical line on the abscissa) were obtained from undercooled phase II samples.

The diffractometric investigation was performed in the temperature ranges 130–540 and 130–470 K for the Na and the K salt, respectively.

With the exception of the low temperature phase III of K propanoate, for which indexing was not successful in spite of several trials, all powder diffraction patterns were similar and led to monoclinic (orthorhombic in phase I of K propanoate) unit cells containing two molecules.

The temperature dependence of the lattice constants is shown in Figs. 2 and 3; in Table 2 smoothed values at a few fixed temperatures are reported.

The X-ray results for phase III of Na propanoate agree with previous dilatometric measurements [2], whereas differences exist for what concerns the molar volume changes in correspondence to sstr's A and B. No satisfactory explanation of such dis-

Table 2. Selected values of the lattice parameters for Na and K propanoate solid phases.

Salt	Phase	<i>T</i> [K]	<i>a</i> [Å]	<i>b</i> [Å]	<i>c</i> [Å]	β [°]
Na propanoate	III	200	3.549	5.310	11.075	94.61
		300	3.573	5.317	11.184	92.82
		400	3.600	5.324	11.313	90.82
		470	3.623	5.328	11.416	(\cong 90)
	II	480	3.621	5.357	11.397	90.30
	I	500	3.623	5.340	11.403	90.75
K propanoate	II	273	3.939	5.799	11.369	93.02
		300	3.957	5.798	11.426	92.22
		350	3.991	5.797	11.531	90.28
	I	355	4.020	5.776	11.613	
		400	4.045	5.768	11.681	
		450	4.073	5.758	11.756	

crepancies was found, in spite of great experimental care. The possibility that the present data refer to metastable phases is to be discarded, since no changes in the patterns were observed after having kept the samples in the pertinent temperature range for reasonably long periods (up to a whole day): moreover, rather fast kinetics for the phase transitions III \rightleftharpoons II and II \rightleftharpoons I in Na propanoate had been revealed by DSC analysis [5].

It is still to be noted that phases I and II of Na propanoate, besides exhibiting very close values of the cell parameters, gave markedly similar diffraction patterns (just slightly differing in the intensity ratios of the reflections).

The single-crystal structure determinations by Lomer et al. [10] on a few K salts indicate bidimensional close packings of carboxylate and alkali ions separated by layers of hydrocarbon chains. On the other hand, the investigations by Gallot and Skoulios [3] on the longer chain homologues put into evidence the influence of the conformational disorder on the long range packing. The cell dimensions determined in the present work are in agreement with the above authors' results: in particular the crystal structure of the phases considered here is of the same type as that termed "lamellaire crystalline" by Gallot and Skoulios. The absence of plastic or mesomorphic phases is clearly a consequence of the lower number of conformational degrees of freedom, while the changes in the lattice constants *a* and *b* (which define the dimensions of the ionic double layer) on passing from the Na to the K salt can satisfactorily be accounted for with the difference of the cationic radii.

- [1] J. J. Duruz and A. R. Ubbelohde, *Proc. Roy. Soc. London* **330 A**, 1 (1972).
- [2] J. J. Duruz, H. J. Michels, and A. R. Ubbelohde, *Proc. Roy. Soc. London* **322 A**, 281 (1971).
- [3] B. Gallot and A. Skoulios, *Koll.-Z. Polym.* **209**, 164 (1966); **210**, 143 (1966); **213**, 143 (1966); **222**, 51 (1968).
- [4] A. R. Ubbelohde, *Melting and Crystal Structure*, Clarendon Press, Oxford 1965.
- [5] P. Ferloni, M. Sanesi, and P. Franzosini, *Z. Naturforsch.* **30a**, 1447 (1975).
- [6] G. Spinolo, V. Massarotti, and G. Campari, to be published.
- [7] P. M. De Wolff, *Acta Cryst.* **10**, 590 (1957).
- [8] O. Kennard, J. D. Hanawalt, A. J. C. Wilson, P. M. De Wolff, and V. A. Frank-Kamenetsky, *J. Appl. Cryst.* **4**, 81 (1971).
- [9] A. Schiraldi and G. Chiodelli, *J. Phys. E: Sci. Instrum.* **10**, 596 (1977).
- [10] T. R. Lomer, *Acta Cryst.* **5**, 11 (1952); J. H. Dumbleton and T. R. Lomer, *ibid.* **19**, 301 (1965).