On the Thermal Behaviour of Li, Na, K and Rb $n.C_5$—$n.C_7$ Alkanoates

M. Sanesi, P. Ferloni, and P. Franzosini
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
della Università, Pavia (Italy)

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DSC analysis allowed to state (between 110 K and the isotropic melt region) the main phase relationships in Li, Na, K and Rb n.pentanoates, n.hexanoates and n.heptanoates. Clearing (when occurring), fusion and solid state transition (when possible) temperatures, and heat effects were measured. The present data are discussed in comparison with those previously collected on higher (up to n.dodecanoates) and lower homologues.

1. Introduction

A series of papers from this laboratory dealt with (i) alkali formates, acetates, propionates and n.butyrates[1], (ii) caesium $n.C_5$—$n.C_{12}$ alkanoates[2], and (iii) Li, Na[3], K[4], Rb[5] long-chain homologues from n.octanoate to n.dodecanoate.

In order to have homogeneous thermal information on all alkali n.alkanoates up to dodecanoates, DSC analysis is now extended to Li, Na, K and Rb salts where the number of carbon atoms is $n_C = 5$, 6 and 7.

Concerning the latter salt group, literature transition temperatures[6], when taken by different investigators, are often poorly agreeing, while, as far as we know, the pertinent ΔH values are completely missing.

2. Experimental

The materials obtained by reaction of Fluka puriss. Li_2CO_3, Merck suprapur Na_2CO_3 and K_2CO_3, and Atomergic Chemetals 99.9% Rb_2CO_3 with Fluka puriss. n.pentanoic ($\geqq 99.5\%$), n.hexanoic ($\geqq 99.5$) and n.heptanoic (> 99) acids were purified as follows. Li salts, after washing with either ethyl ether or acetone, were dissolved in methanol and fractionally precipitated by addition of 2-propanol; Na salts, similarly washed, were twice re-crystallized from methanol (Na n.pentanoate) or ethanol; K (after washing) and Rb salts were re-crystallized from 2-propanol.

Details on the experimental procedure were the same as previously described[1].

3. Results and Discussion

3.1. Clearing (when present) and fusion temperatures (T_{Cl}/K and T_F/K, respectively) and enthalpies (ΔH_{Cl}/kcal mole^{-1} and ΔH_F/kcal mole^{-1}, respectively) of the investigated n.pentanoates, n.hexanoates and n.heptanoates are summarized in Table 1.

Concerning solid state transitions (sstr), only T_{sstr}/K and ΔH_{sstr}/kcal mole^{-1} values judged as fully satisfactory are reported in Table 2, whereas data of poor trustworthiness (due to excessive thermal inertia, peak unsharpness, etc.) were excluded from tabulation, though incidentally mentioned in the text hereafter.

LiC_5—LiC_7 (for the sake of simplicity, the n.alkanoate where $n_C = a$ is from now on indicated as MC_a, M being the proper alkali metal) exhibited fusion points which were (i) decreasing as n_C increased, and (ii) somewhat higher than, though sufficiently close to those given in Ref. [6d]. Previously unknown sstr's were put into evidence in the pentanoate and heptanoate.

The trend of T_{Cl} and T_F in Na salts is discussed in detail in 3.3, while only a few peculiarities of the NaC_5 and NaC_6 melting processes are to be mentioned here. Concerning NaC_5, fusion (into a mesomorphic liquid) of a sample scanned for the first time was always followed by a small heat emission, which could not be detected in any subsequent heating run. As a possible explanation, unstable structures might be supposed to be present in the solid coming from the adopted purification process and not in that obtained by cooling the mesomorphic liquid. Anyway, first run DSC traces were not employed for ΔH_F evaluation. First heating of NaC_6 samples gave (in the neighborhood of 500 K) unsharp endothermic effects,

Reprint requests to Prof. Paolo Franzosini, Istituto di Chimica-Fisica e di Elettrochimica della Università, Viale Taramelli 16, *I-27100 Pavia* (*Italy*).

Table 1. Clearing and fusion temperatures and enthalpies (The number of significant figures depends in each case on the reproducibility of the pertinent experimental data).

salt	tr	T_{tr} K	ΔH_{tr} kcal mole^{-1}
LiC_5	F	576.0 ± 0.2	5.06 ± 0.04
LiC_6	F	562	5.69 ± 0.08
LiC_7	F	550	6.06 ± 0.06
NaC_5	Cl	631 ± 4	0.47 ± 0.03
	F	498 ± 2	2.60 ± 0.03
NaC_6	Cl	639.0 ± 0.5	0.40 ± 0.03
	F	499.6 ± 0.6	2.59 ± 0.05
NaC_7	Cl	642 ± 2	0.36 ± 0.02
	F	509 ± 2	2.16 ± 0.04
KC_5	Cl	716 ± 2	1.15 ± 0.05
	F	586.6 ± 0.7	3.7
KC_6	Cl	725.8 ± 0.8	1.0
	F	581.7 ± 0.5	4.03 ± 0.08
KC_7	Cl	722 ± 3	0.82 ± 0.02
	F	571.3 ± 0.9	4.22 ± 0.04
RbC_5	Cl	703 ± 2	1.24 ± 0.06
	F	640.1 ± 0.5	2.60 ± 0.02
RbC_6	Cl	723 ± 2	1.11 ± 0.05
	F	615.4 ± 0.7	2.47 ± 0.02
RbC_7	Cl	724.4 ± 0.8	1.0
	F	600	2.70 ± 0.08

Table 2. Solid state transition temperatures and enthalpies (The number of significant figures depends in each case on the reproducibility of the pertinent experimental data).

salt	T_{tr} K	ΔH_{tr} kcal mole^{-1}
LiC_5	201 ± 2	0.34 ± 0.02
LiC_7	317.9 ± 0.8	1.36 ± 0.02
NaC_6	473 ± 2	0.22 ± 0.03
	386 ± 2	0.35 ± 0.03
KC_5	399.5 ± 0.9	0.11 ± 0.02
KC_7	345.4 ± 0.6	1.31 ± 0.05
	332.0 ± 0.8	1.15 ± 0.05
RbC_5	502.7 ± 0.4	1.20 ± 0.03
	258 ± 2	0.87 ± 0.02
RbC_6	515.9 ± 0.9 526.0 ± 0.4	0.65 ± 0.02
	241 ± 2	0.74 ± 0.08
RbC_7	320.1 ± 0.8	$2,12 \pm 0.03$

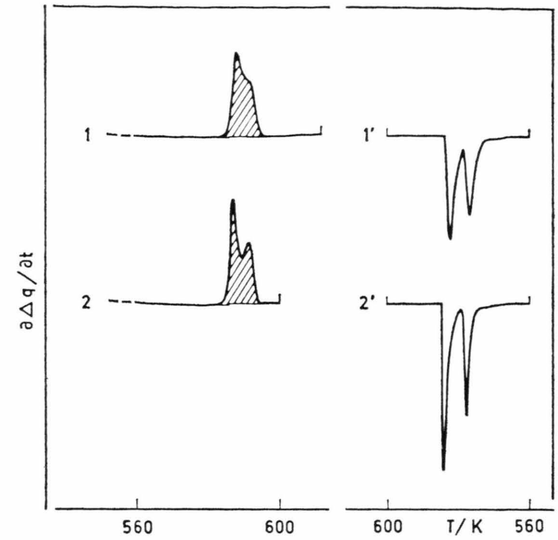

Fig. 1. Fusion and crystallization of a KC_5 sample. Curves 1,1': second heating and cooling runs (sensitivity range, $r = 10$; scan speed, $s = 10$ K min^{-1}; chart speed, $c = 20$ mm min^{-1}). Curves 2,2': third heating and cooling runs ($r = 5$; $s = 5$; $c = 10$). The hatched areas were employed for ΔH evaluation: for further explanation see text.

whereas during any subsequent run two well reproducible though almost completely overlapping peaks were recorded, of which the sharper and by far the larger one was the second, to be attributed to fusion: separation attempts having been unsuccessful, the whole enthalpy change involved was however reported as ΔH_F in Table 1.

Minor endothermic pen deflections were also observed (on heating) in each of the three sodium homologues at $350 < T/K < 500$, though quantitative data could be taken only in the case of NaC_6 (sstr at 473 ± 2 K, to be compared with those reported in Refs. [6a] and [6c] at 480 and 483 K, respectively, and sstr at 386 ± 2 K).

For KC_5-KC_7 and RbC_5-RbC_7, melting temperatures by previous investigators [6c,d] proved to be in sufficient agreement with the present ones, whereas the sets of clearing points from Ref. [6d] are significantly lower.

Potassium *n*.pentanoate samples behaved on melting in the same way as sodium *n*.hexanoate, although exhibiting peak areas not very different from each other and a better resolution when cooled (see Figure 1). Once more, however, we thought it convenient to tabulate as ΔH_F the whole heat effect comprehensive of fusion and of the close-to-fusion phenomenon (possibly a sstr), and as T_F the temperature of the latter.

Besides the tabulated sstr's, a few other, poorly reproducible, endothermic pen deflections were recorded on heating, among which one occurring in KC_6 in the neighborhood of 250 K can be mentioned.

3.2. In order to give a comprehensive picture of the phase relationships in the Li, Na, K and Rb *n*.alkanoates families, the Cl, F and sstr temperatures of Tables 1 and 2 are drawn in Figs. 2–5

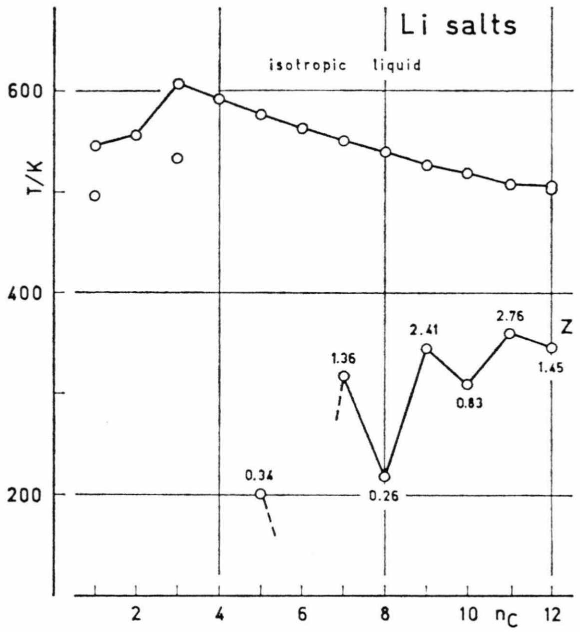

Fig. 2. Phase transition temperatures in Li $C_1-n.C_{12}$ alkanoates. The figure attached to each Z point indicates the relevant heat effect in kcal $mole^{-1}$.

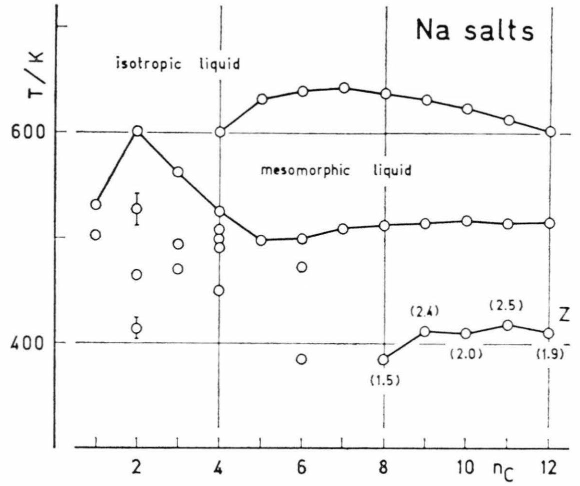

Fig. 3. Phase transition temperatures in Na $C_1-n.C_{12}$ alkanoates. The figure attached to each Z point indicates the relevant heat effect in kcal $mole^{-1}$.

together with those previously taken[1,3-5] on the higher (up to $n.C_{12}$) and lower homologues.

The information is complete for what concerns clearing and fusion, the former being absent in the Li series, and starting from NaC_4, KC_4 and RbC_5 in the sodium, potassium and rubidium ones respectively, although the sodium salts situation deserves further comments (see 3.3). As for the sstr's, the information given is thought to be complete for Li salts, whereas lacks are existing, as specified in 3.1 and Refs. [1,3-5], in particular in the case of phase transitions occurring (for the Na, K and Rb higher homologues) in the so-called waxy region.

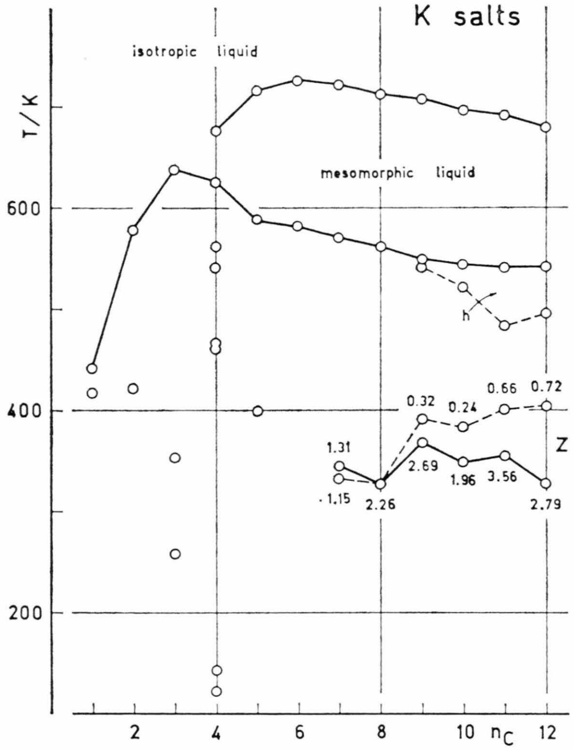

Fig. 4. Phase transition temperatures in K $C_1-n.C_{12}$ alkanoates. The figure attached to each *Z* pont indicates the relevant heat effect in kcal $mole^{-1}$. The letter **h** denotes the 'hump' region[4].

An odd-even alternating effect, absent or hardly perceivable in clearing and fusion temperatures, impressively occurs in the sstr sequences indicated as *Z*. Moreover, going from the higher to the lower homologues the involved heat effect tends (in each series) to become smaller and smaller, although that pertinent to each odd homologue is usually larger than those of its even neighbors.

The longest sequence, covering the range from dodecanoate to butyrate, could be put into evidence in the Rb series, whereas a satisfactory experimental evidence for *Z* sstr's could not be obtained with K salts when $n_C < 7$, and with Na salts when $n_C < 8$. Concerning the Li series, should a parabola be drawn through the sstr temperatures of LiC_{12},

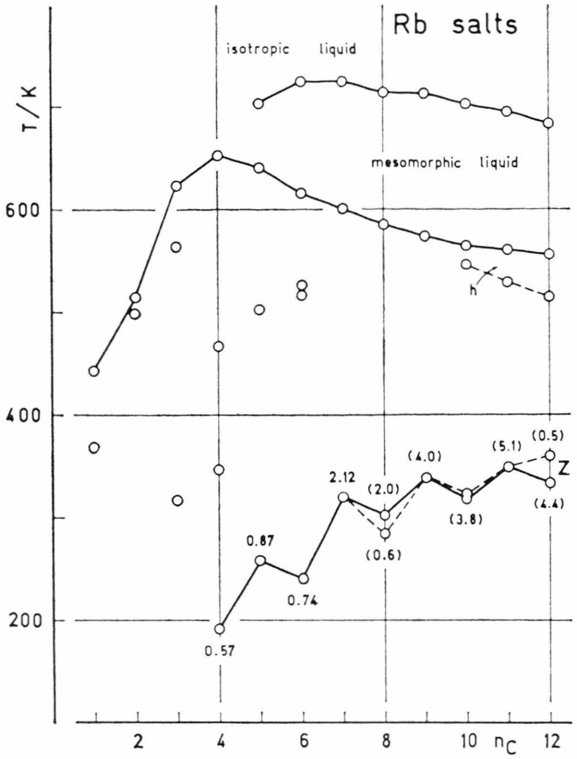

Fig. 5. Phase transition temperatures in Rb $C_1-n.C_{12}$ alkanoates. The figure attached to each *Z* point indicates the relevant heat effect in kcal mole^{-1}. The letter **h** denotes the 'hump' region[5].

LiC_{10} and LiC_8, a sstr at $T/K < 110$ (i.e., outside the investigated range) is reasonably to be expected for LiC_6: therefore, this sstr sequence may be supposed to cover the interval from dodecanoate to (at least) pentanoate.

It is still to be noted that the sstr's under discussion are mostly single, but may be twinned for a number of K and Rb salts: solid and dashed lines connect in Figs. 4 and 5 the points concerning the larger and the smaller peaks, respectively.

3.3. Melting processes were more extensively studied in the sodium homologues than in any other *n*.alkanoate family. Opinions of different investigators being, however, somewhat conflicting, a comparison of Ref. [6] T_{Cl} and T_F data among themselves and with our results seems worthy of some comment.

Let us consider Figure 6. Concerning the T_{Cl} trend, it can be said that [apart from the earlier (1941) measurements by Vold et al. [6a]] Ref. [6b] (1961), Ref. [6c] (1970), Ref. [6d] (1972) and the work from this laboratory concordantly allow to evidence the following points: (i) a mesomorphic liquid phase exists starting from Na butyrate *; (ii) T_{Cl} gradually increases from ~ 600 K when $n_C = 4$ to $T/K > 630$ when $n_C = 7$, and then progressively decreases down to ~ 560 K when $n_C = 18$. Further, from the above sources (including [6a]) it is possible to outline a T_F trend characterized by a sharp maximum when $n_C = 2$, followed by a minimum in correspondence to $n_C = 5$ or 6.

Quite different trends, however, in particular for what concerns T_{Cl}, were reported in a recent (1976) paper by Roth et al.[6e], who also claimed the existence of a mesomorphic liquid phase in Na propionate, in the range 545–561 K. No immediate explanation can be given for such rather surprising discrepancies, which anyway are largely outside

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* For the sake of completeness, it is to be said that, as a provisional result, Ubbelohde et al. [7] (1970) mentioned also for Na propionate "a fugitive mesophase extending only 1° above the melting point", the existence of which was not confirmed in subsequent papers [6d, 8].

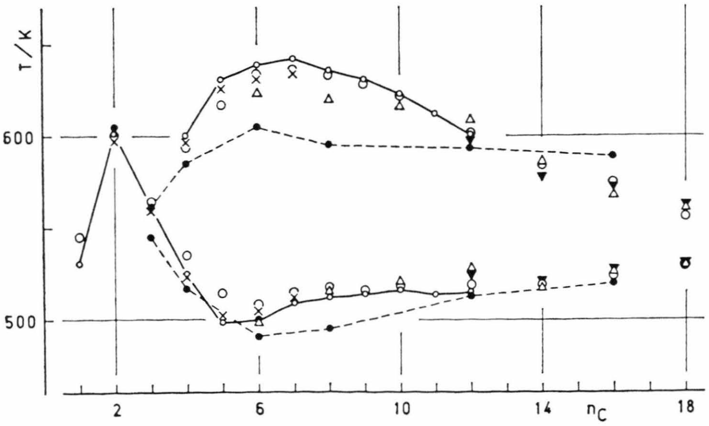

Fig. 6. Comparison among clearing and fusion temperatures from different sources in Na $C_1-n.C_{18}$ alkanoates. Small empty circles, connected by solid lines: work from this laboratory; empty triangles: Ref.[6a] (1941); filled triangles: Ref.[6b] (1961); large empty circles: Ref.[6c] (1970); crosses: Ref.[6d] (1972); filled circles, connected by dashed lines: Ref.[6e] (1976).

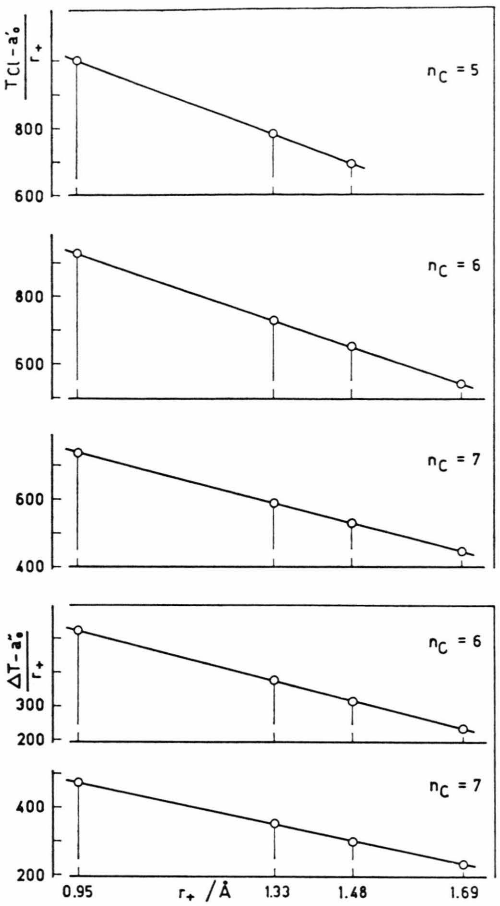

Fig. 7. Upper section: T_{Cl} dependence on r_+ for alkali $n.C_5-n.C_7$ alkanoates (T_{Cl}/K values from Ref.[2] and Table 1; $a_0' = -321.37$, -241.26, -59.45 for $n_C = 5$, 6, 7, respectively). Lower section: ΔT dependence on r_+ for alkali $n.C_6$, $n.C_7$ alkanoates ($a_0'' = -356.69$, -316.91 for $n_C = 6$, 7, respectively). The r_+ values for Na^+, K^+, Rb^+ and Cs^+ are from Ref.[9].

the usual experimental uncertainties of the thermal measurements.

3.4. With regard to clearing and to the width of the mesomorphic liquid range ($\Delta T = T_{Cl} - T_F$), two remarks can still be made.

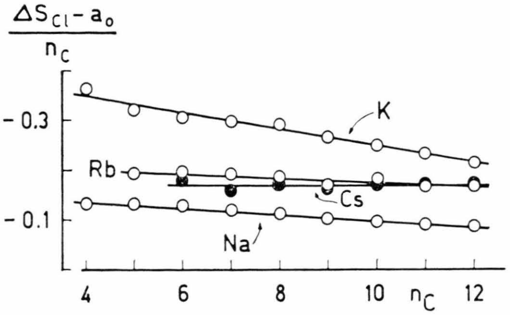

Fig. 8. Parabolic ΔS_{Cl} dependence on n_C for Na, K and Rb n.alkanoates ($a_0 = 1.402$, 3.217, 2.717, respectively). The linear dependence for Cs salts is also shown ($a_0 = 2.733$). Data were taken from Refs.[1–5] and Table 1.

(i) In the alkali n.alkanoate series formed with different cations and a common anion where $8 \leqq n_C \leqq 12$, it was already shown[5] that, for a given n_C, the T_{Cl} and ΔT trends vs. the cationic radius (r_+/Å) were formally described by parabolic equations: the same holds when $n_C = 6$ and 7 too, as it may be seen in Figure 7. In the upper part of the Figure, the parabola going through the three points pertinent to Na, K and Rb pentanoates is also drawn. Introducing $r_{Cs^+} = 1.69$ Å into the parabolic equation gives $T_{Cl} = 640.5$ K: this is 15 K below the observed melting point of Cs pentanoate, consistently with the experimental fact that in this salt no mesomorphic liquid phase occurs[2].

(ii) Increasing n_C causes both the ΔH_{Cl}'s and ΔS_{Cl}'s to decrease in each alkali salt series. In particular, the ΔS_{Cl} trend can be formally described by parabolas when $M =$ Na, K, Rb (see Fig. 8, where the linear trend pertaining to Cs salts[2] is also shown).

Acknowledgements

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[1] P. Ferloni, M. Sanesi, and P. Franzosini, Z. Naturforsch. **30a**, 1447 (1975).

[2] M. Sanesi, P. Ferloni, M. Zangen, and P. Franzosini, Z. Naturforsch. **32a**, 285 (1977).

[3] P. Ferloni, M. Zangen, and P. Franzosini, Z. Naturforsch. **32a**, 627 [1977].

[4] P. Ferloni, G. Spinolo, M. Zangen, and P. Franzosini, Z. Naturforsch. **32a**, 329 [1977].

[5] P. Ferloni, M. Zangen, and P. Franzosini, Z. Naturforsch. **32a**, 793 [1977].

[6] Main references: (a) M. J. Vold, M. Macomber, and R. D. Vold, J. Amer. Chem. Soc. **63**, 168 [1941]; (b) A. E. Skoulios and V. Luzzati, Acta Cryst. **14**, 278 (1961); (c) E. Baum, D. Demus, and H. Sackmann, Wiss. Z. Univ. Halle XIX '70, 37; (d) H. J. Michels and A. R. Ubbelohde, J. C. S. Perkin II, 1879 [1972]; (e) J. Roth, T. Meisel, K. Seybold, and Z. Halmos, J. Thermal Anal. **10**, 223 [1976].

[7] A. R. Ubbelohde, H. J. Michels, and J. J. Duruz, Nature **228**, 50 [1970].

[8] J. J. Duruz, H. J. Michels, and A. R. Ubbelohde, Proc. Roy. Soc. Lond. **A 322**, 281 [1971].

[9] G. J. Janz, "Molten Salts Handbook", Academic Press, New York, 1967.