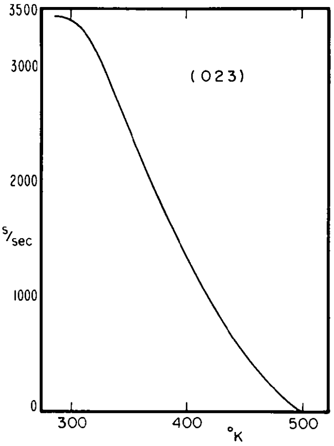

Fig. 1. Intensity of the 023 reflection of $Cs_2NaFe(CN)_6$ as a function of temperature.

can, by virtue of the high critical temperature for the phase II–phase III transition, be obtained in both the tetragonal and monoclinic phases, thereby allowing direct confirmation of the phase II *P*4/*mnc* space group. The cubic to tetragonal phase change observed in the earlier study of $Cs_2LiCr(CN)_6$ is therefore shown, by analogy to the present work, to be an antiferro displacive rotation of the $M(CN)_6^{3-}$ octahedra about the cubic *c* axis as was previously inferred.

Raman spectral data show that the tetragonal → monoclinic phase change in $Cs_2LiM(CN)_6$ salt is 2nd order involving a soft Cs^+ ion translational mode. A plot of the intensity of the 023 reflection for $Cs_2NaFe(CN)_6$ as a function of temperature is shown in Fig. 1. The intensity of this reflection decreases continuously and reversibly to zero intensity at $T_c^2 = 498$ K, as is consistent with a higher-order phase change. Thus, it is likely that the $Cs_2NaFe(CN)_6$ structural change in the vicinity of T_c^2 derives from the same soft Cs^+ translational mode implicated in earlier studies of $Cs_2LiM(CN)_6$ salts. We note, however, that the room-temperature structure of the Na salt (Fletcher & Gibb, 1977) exhibits additional distortions not present in the room-temperature structure of $Cs_2LiCr(CN)_6$. These added distortions from the parent *Fm*3*m* cell correspond to $Fe(CN)_6^{3-}$ rotary and Cs^+ translational symmetry coordinates which also transform as the totally symmetric representation in the $P2_1/n$ cell. Apparently, as the Na crystals are cooled well below T_c^2 the frequency of the soft mode approaches those of other A_1 modes thereby resulting in enhanced mixing and a change in the character of the soft mode.

The critical temperature observed for the Na salt is much higher than those observed for the analogous phase change in the $Cs_2LiM(CN)_6$ salts, as is consistent with the notion that the lattice instabilities result from the Cs^+ ion occupying too large a site in the *Fm*3*m* cell. As the Cs^+ site size increases, the cubic structure becomes less stable thereby driving T_c^1 and T_c^2 to higher temperatures. From the *c* axis length in the tetragonal phase of $Cs_2NaFe(CN)_6$ we estimate a Cs—N nearest neighbor contact distance of *ca* 3·89 Å in the hypothetical *Fm*3*m* phase of the sodium salt. It is striking that in going from $Cs_2LiFe(CN)_6$, where the Cs—N distance is 3·762 Å (Swanson & Ryan, 1973), to the Na salt T_c^2 increases about 330 K.

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On the existence of low- and high-temperature crystal forms of lithium polyphosphate.

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Abstract

The existence of two crystal forms of lithium polyphosphate $[(LiPO_3)_x.H_2O]$ obtained on crystallization during polymerization of LiH_2PO_4 is confirmed. The different structures occur on growth below or above about 523 K. The transition from the low-temperature to the high-temperature form proceeds very slowly so that differential thermal analysis can only detect it as a very shallow endotherm, peaking at 857 K at a 20 K min^{-1} heating rate. The transition is irreversible and does not occur on cooling. The low-temperature crystal form results from crystallization during polymerization of double PO_4^- tetrahedra to a twisted zigzag chain conformation. Upon annealing, an intramolecular rearrangement

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leads to the high-temperature crystal form which has a five-PO_4^--tetrahedra repeat, arranged in a similar irregular, but shortened zigzag conformation.

The existence of two crystal forms of $(LiPO_3)_x.H_2O$ grown from the monophosphate LiH_2PO_4 was first observed by Thilo & Grunze (1955) based on X-ray diffraction patterns. The two forms were found to occur below and above 523 K, respectively. Those first results, however, were not mentioned in more recent reviews (Thilo, 1962; Corbridge, 1966). Detailed crystal structure determinations of other selected polyphosphates were made later by Corbridge (1956) and Jost (1961, 1963, 1964). A crystal structure of $LiPO_3$ was studied by Grenier & Durif (1973) and finally solved by Guitel & Tordjman (1976). Recent investigations of ours into crystallization during polymerization resulted in a detailed description of the nucleation of lithium polyphosphate crystals by oligophosphates, their growth mechanism by dimer addition, and the crystallization and melting of prepolymerized polymer molecules (Benkhoucha & Wunderlich, 1978*a*,*b*,*c*).

Table 1. *Observed reflections for the high- and low-temperature forms of* $(LiPO_3)_x.H_2O$

$LiPO_3(t)$[a]		$LiPO_3(h)$[b]	
d_o (Å)[c]	Intensities[d]	d_o (Å)[c]	Intensities[d]
2·89 –	*vw*	2·86 (204)	*vs*
2·71 $(40\bar{1})$	*vw*	2·79 (014) (412)	*m*
2·61 $(13\bar{1})$	*w*	2·46 (022)	*vs*
2·56 –	*m*	2·34 (222) (404)	*w*
2·44 $(20\bar{2})$	*s*	2·03 $(51\bar{5})$	*w*
2·37 (400) (040)	*vs*	1·85 (802) (025)	*vs*
2·22 $(40\bar{2})$	*vw*	1·80 (424)	*vw*
2·15 $(22\bar{2})$	*vw*	1·72 $(52\bar{5})$	*vs*
1·98 $(42\bar{2})$	*w*	1·45 (408)	*m*
1·86 (112)	*m*	1·37 (040)	*w*
1·82 –	*m*	1·21 (045)	*w*
1·69 (440)	*vs*	1·17 (444)	*s*
1·64 (421)	*w*	1·16 $(54\bar{5})$	*m*
1·60 (060) $(44\bar{2})$	*s*	1·12 (840)	*w*
1·53 (260)	*s*	1·11 $(10,0,\bar{1}\bar{0})$	*w*
1·45 –	*vw*	1·04 (10,4,10)	*s*
1·37 –	*vw*	0·92 (0,4,10)	*w*
1·31 (402)	*w*	0·92 (0,4,10)	*w*
1·24 (062)	*m*	0·89 (848)	*w*
1·21 $(40\bar{4})$	*w*	0·88 –	*w*
1·17 (800) (080)	*vw*		
1·16 $(20\bar{4})$	*vw*		
1·12 $(22\bar{4})$	*m*		
1·11 $(11\bar{4})$	*w*		
1·04 $(24\bar{4})$	*m*		
1·03 –	*vw*		
1·02 –	*vw*		
1·00 (114)	*vw*		
0·93 –	*vw*		
0·92 –	*vw*		
0·90 –	*w*		
0·89 –	*vw*		
0·88 (244)	*w*		

(*a*) Indexed tentatively according to the $LiAsO_3$ structure of Hilmer & Dornberger-Schiff (1956). (*b*) Indexed tentatively according to the structure determined by Guitel & Tordjman (1976). (*c*) Filtered Cu radiation, λ = 1·54 Å. (*d*) Intensities: *vs*, very strong; *s*, strong; *m*, medium; *w*, weak; *vw*, very weak.

During the course of our work, we confirmed the existence of the two crystalline forms. Their powder patterns are illustrated in Fig. 1 and Table 1 to enable identification of the samples. The crystal structure solved by Guitel & Tordjman (1976) agrees only with that of our data of the high-temperature form. Crystals grown by crystallization during polymerization at 513 K have a distinctly different X-ray diffraction pattern from those grown at, for example, 723 K. Differential thermal analysis (DTA) of the low-temperature form, however, did not show the expected crystal–crystal transition at about 523 K on heating. Up to 773 K no endotherm was observed and the X-ray diffraction pattern had not changed after cooling to room temperature. Only on prolonged heating (several hours) of the low-temperature form at much higher temperature (*i.e.* 3 h at 673 K) could we accomplish a change in the diffraction pattern from the low- to the high-temperature crystal form. On heating at 20 K min^{-1}, a shallow endotherm, attributed to the solid–solid transition, occurs at 857 K. Once obtained, the high-temperature form did not change back to the low-temperature form on cooling. An attempt to revert to the low-temperature form by very slow cooling from 623 K to room temperature over 4 d failed. An occasional endotherm, found at 588 K on DTA of the low-temperature crystal form, was ultimately attributed to melting of unreacted diphosphate crystals which are sometimes present in small quantities, but could always be removed by extraction with water.

No detailed crystal structure determination of the low-temperature crystal form has been made, but the crystal structure can be deduced from information on isomorphism and unit-cell data. The low-temperature crystal form of $LiPO_3$ was found by Thilo & Grunze (1955) to be

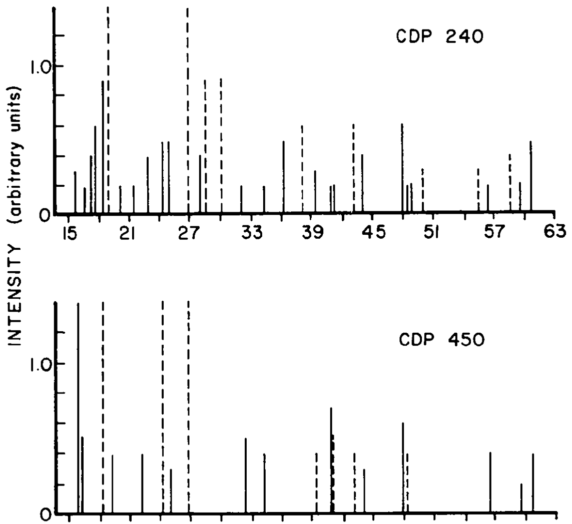

Fig. 1. X-ray diffraction peaks for crystals grown at 513 K and at 723 K. Dashed lines represent peaks observed in both this work and by Thilo & Grunze (1955).

isomorphous with $LiAsO_3$. The $LiAsO_3$ crystal structure was determined by Hilmer & Dornberger-Schiff (1956) [monoclinic, a = 10·18, b = 9·43, c = 5·25 Å (chain axis), β = 110·53°, Z = 8, density = 3·655 Mg m^{-3}]. The macromolecular chain in $LiAsO_3$ has a twisted two-AsO_4^--tetrahedra repeat. A similar chain conformation was observed by Jost (1963) for KPO_3 [monoclinic, a = 14·02, b = 4·54 (chain axis), c = 10·28 Å, β = 101·5°, Z = 8, density = 2·446 Mg m^{-3}]. The average P—P distance of adjacent PO_4^- tetrahedra within the chain is 2·83 Å in the KPO_3 crystal. The PO_4^- tetrahedra are characterized by an average P—O bond length of 1·603 Å along the chain and the POP and OPO bond angles of 131 and 98°. A comparison of the Debye patterns of $LiAsO_3$ and the low-temperature crystal form of $LiPO_3$ as given, for example, by Thilo & Grunze (1955) reveals that the first four strong diffraction lines (400, 440, 060, and 260, see Table 1) are similar. Assuming thus that the a projection and the b axis are close in $LiAsO_3$ and the low-temperature form of $LiPO_3$, we used the observed 400, 440 and 402 reflections of the low-temperature form of $LiPO_3$ and the extrapolated $LiPO_3$ density of Thilo & Grunze (1955) of 2·627 Mg m^{-3} to calculate the following monoclinic unit-cell parameters: a = 10·7, b = 9·5, c = 4·8 Å (chain axis), β = 118°, 8 $LiPO_3$ per unit cell.

Table 1 shows the tentative identification of the major reflections for the hypothetical unit cell. The standard deviation of 21 calculated *versus* measured Bragg distances is ±0·03 Å. The two-PO_4^--tetrahedra repeat length of the low-temperature form of $LiPO_3$ is thus only slightly larger than in KPO_3.

The high-temperature crystal form was found by Thilo & Grunze (1955) to be similar to Li_2SiO_3. A comparison of the Debye pattern with calculated spacings of the $LiPO_3$ structure of Guitel & Tordjman (1976) shows that these authors analyzed the high-temperature crystal form (see Table 1, 22 reflexions, average error −0·002, standard deviation ±0·014 Å) {monoclinic, a = 16·453, b = 5·405, c = 13·086 Å, β = 98·99°, Z = 20, density = 2·482 Mg m^{-3}, chain axis along $[10\bar{1}]$ with a five-PO_4^--tetrahedra repeat length of 9·678 Å}. The average P—P distance of adjacent PO_4^- tetrahedra within the chain is 2·94 Å. The PO_4^- tetrahedra are characterized by an average P—O bond length of 1·598 Å along the chain and POP and OPO bond angles of 134 and 101°. The high-temperature form of $LiPO_3$ contains thus a shortened chain conformation of similar PO_4^- tetrahedra as in the low-temperature crystal form, obtained by rotation around the P—O bonds.

The experimental evidence on the interconversion of the two crystal forms could be explained by assuming that the high-temperature crystal form is also stable at low temperatures. On heating, the metastable low-temperature form converts, after gaining sufficient thermal motion, to the stable high-temperature form. Cooling, of course, would then not regenerate the metastable structure. The assumption of a high-temperature form, stable at low temperature is, however, in contradiction with the findings of Thilo & Grunze (1955) that the low-temperature form has a higher density, a fact which we could confirm. Since the rotational energies of the PO_4^- tetrahedra are low (Semlyen & Flory, 1966), intramolecular considerations could not overcome packing considerations and one would expect that the most dense crystal is also the most stable at a sufficiently low temperature. One must turn to another reasoning. We assume the low-temperature form to be the more stable crystal form at low temperatures. On heating, a less dense, shortened, irregular zigzag chain conformation becomes more stable because of its higher entropy. The transition involves, however, an intramolecular rearrangement throughout the crystal which is often slow. The experiments show that the transition needs a sizable superheating. For the reverse transition, a similar supercooling may be needed, which brings the system to a temperature range where the transition is practically impossible, thereby making it irreversible. The transition under discussion would then be similar to the α–β transition in poly-*p*-xylylene. The stable form is the monoclinic α-form (Iwamoto & Wunderlich, 1973). On heating above 493 K, the α-crystals change to the high-temperature, trigonal β-form which is, as in the present case, difficult to revert back to the α-form on cooling (Niegisch, 1971).

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