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# PHASE TRANSITIONS CRYSTALLINE TO PLASTIC-CRYSTALLINE AND THE SPECIFIC HEAT OF $M_3P_7$ COMPOUNDS (M = Li, Na, K, Rb, Cs)

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## ABSTRACT

Heat capacities of the trialkaliheptaphosphides $M_3P_7$ (M=Li...Cs) have been measured in the range 120-770K in closed alumina pans. Temperatures $T_c$, enthalpies $\Delta H_c$, and entropies $\Delta S_c$ of the crystalline to plastic-crystalline phase transitions have been determined. The nature of the first order transition is proofed by a hysteresis in $T_c$, a jump in specific heat, no space group - subgroup relationship and a volume jump of 8% at $T_c$. The melting points $T_m$, the melting enthalpies $\Delta H_m$ and entropies $\Delta S_m$ have been estimated from DTA measurements in closed quartz ampoules. The $T_c$ values are related to binding energies. For all compounds the $\Delta S_c$ values are larger than $\Delta S_m$, which is in agreement with theoretical considerations and proof the nature of the phase transitions.

## INTRODUCTION

The electropositive metals form with phosphorus a lot of binary compounds, which are built up by cations and isolated, one-, two-, and threedimensional polyanions. Because of their fascinating chemical reactions (ref.1) as well as their physical properties (ref.2), their high thermal stability (ref.3) and their dynamic behaviour in solvents at the n.m.r. time scale (ref.2,4), a thermoanalytical characterisation of the compounds with the compositions M:P = 3:7 seems to be necessary for a better understanding of chemical and physical properties. All compounds $M_3P_7$ consist of the $P_7^{3-}$ cage, isoelectronic to $P_4S_3$ (ref.5) and crystallize in different forms. The bonding within the $P_7$ cages is covalent, the cages are connected by partially ionic bonds via the alkali metals. As most of the plastic crystals investigated so far are of the molecular type, the appearance of plastic phases with ionic components is noteworthy.

## EXPERIMENTAL

The compounds $M_3P_7$ have been prepared by synthesis of stochiometric amounts of alkali metals and red amorphous phosphorus at 800-1000K in sealed niobium and tantalum containers. They have been purified by high vacuum sublimation. Due to their large sensitivity against oxygen and moisture, the samples are prepared in cold sealed alumina pans with 10-30 mg of substance.

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Special care was taken to proof the unchanged nature of the samples after several measuring runs. The specific heat data as well as the heat of transitions have been recorded on a differential scanning calorimeter (Perkin Elmer DSC-2) in the range 120-770K with heating rates of 10K/min. One compound ($Rb_3P_7$) shows severe undercooling, leading to an oscillating back transition. This problem as well as strong variation of the line shapes, due to reduced thermal conductivity of the material, are overcome by varying sample sizes and heating rates. The melting points and enthalpies are estimated from DTA measurements (DTA 404 S Netzsch) in closed quartz ampoules making use of enthalpy ratios between the crystalline - plastic crystalline and the solid-liquid phase transitions. The crystal structures of the compounds $Li_3P_7$, $Na_3P_7$, and $Cs_3P_7$ have been determined by single crystal X-ray methods (ref.1-3)(fig.1). Table 1 contains the essential thermodynamic parameters. In fig. 2 the specific heat $c_p$ vs. T and the crystalline to plastic crystalline phase transitions are displayed.

## RESULTS AND DISCUSSION

The five homologous compounds undergo first order phase transitions from a crystalline, low temperature phase (LT) from different space groups to a plastic crystalline high temperature phase (HT) with the common space group Fm3m. This is clearly proofed by the observed hysteresis as well as the crystallographic details. As can be seen in fig. 1, the alkali metals have to make only small displacements to reach the highly symmetric sites of the plastic crystalline phase. All compounds (except $Li_3P_7$) adopt in the HT phase the sites of the intermetallic parent phase $Li_3Bi$, where the gravicenters of the $P_7$ cages occupy the Bi-positions in space group Fm3m. There is no space group - subgroup relationship between the observed space groups, which is a further proof for the first order nature of transitions. Another feature are the observed jumps in the specific molar volume. Above $T_c$ the volumes are approximately 8% larger with respect to the specific molar volumes at room temperature. In comparison to a typical molecular plastic crystal like $\beta$-$P_4S_3$ (isoelectronic to $P_7^{3-}$) where the jump is 14%, these values are considerably smaller. In all compounds $\Delta S_c >> \Delta S_m << 20$ J/molK is valid, which is a characteristic property of plastic crystalline phases and corresponds to a premelting of the compounds at $T_c$. The calculation of the distances of the gravicenters of the $P_7$ groups yield values of 7.15 Å (Na), 7.50 Å (K), 7.65 Å (Rb), and 7.90 Å (Cs). In comparison to a maximum diameter of 7.4 Å for a rotating $P_7$ cage this explains the decrease in $T_c$ down to $Rb_3P_7$. The increase of $T_c$ for $Cs_3P_7$ might be explained by the large polarisability of Cs (ref.6). The same non-continous relation (going from Na to Cs) is observed for the order-disorder transition temperatures of the alkalimetal cyanides and we

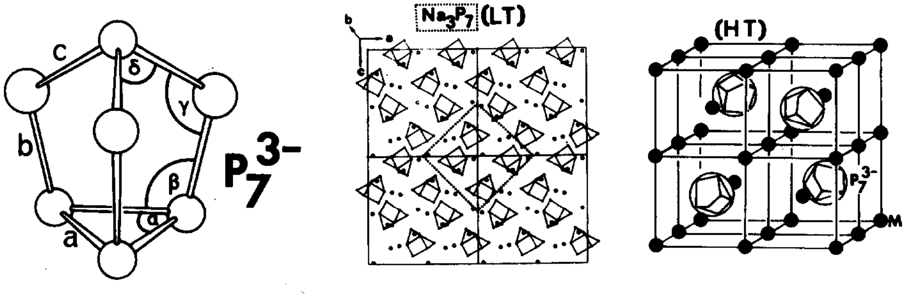


Fig. 1. left: $P_7^{3-}$ anion in compounds $M_3P_7$. Typical values for bond distances are a=2.24 Å, b=2.18 Å, c=2.18 Å, $\alpha=60^0$, $\beta=103^0$, $\gamma=99^0$, $\delta=102^0$. center: Four unit cells of crystalline LT-$Na_3P_7$. The position of the plastic crystalline unit cell is indicated by dotted lines. Note the small displacements of the alkali metals from the ideal positions. right: The intermetallic parent phase $Li_3Bi$, where the Bi atoms are replaced by the centers of mass of the $P_7$ anions.

emphasize that the ratio between melting and boiling temperature of the pure alkali metals behave the same. The $T_c$ values and the binding energies $\Delta E_b$, which are related to the distance d between metal M and phosphorus P $\Delta E_b \sim d^{-1}(M{-}P)$, are plotted in fig. 3 and show also such an anomaly. In contrast to these variations of the physical and thermal parameters as function of the alkali metal (see tab.1) the melting points $T_m$, the melting enthalpies and entropies are nearly identical for all compounds: 1210 K < $T_m$ < 1260 K, 7 $kJmol^{-1}$ < $\Delta H_m$ < 14 $kJmol^{-1}$. This result is in agreement with regarding the crystalline plastic-crystalline phase transitions as premelting.

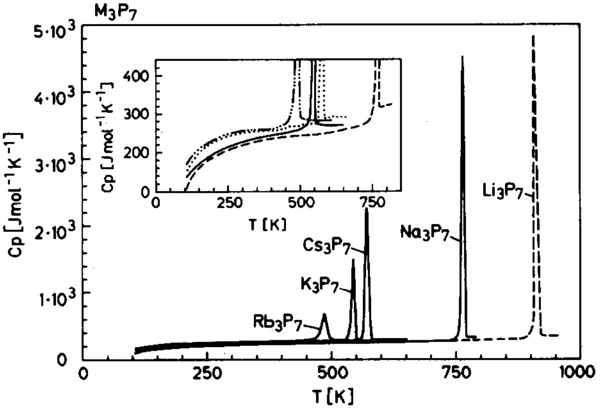
The Debye-temperatures $\Theta_D$, calculated from the $c_p$ data, are approximately 460 K for $Na_3P_7$ and $K_3P_7$ and ca. 310 K for $Rb_3P_7$ and $Cs_3P_7$ in the temperature range from 100 to 250 K, respectively (fig.2). The rather marked separation

Table 1: Transition temperatures, enthalpies, entropies and c values. The index c denotes the crystalline - plastic crystalline, index m the solid - liquid phase transition. The dimensions are: T [K], H [kJ/mol], S and $c_p$ [J/molK], heating ↑ and cooling ↓.

| M | $T_c\uparrow$ | $T_c\downarrow$ | $\Delta H_c\uparrow$ | $\Delta H_c\downarrow$ | $\Delta S_c\uparrow$ | $T_m^*$ | $\Delta H_m^*$ | $\Delta S_m^*$ | $\sum\Delta H$ | $\Delta c_p$ (e.s.d.) |
|---|---|---|---|---|---|---|---|---|---|---|
| Li | 900* | 833* | >36* | - | 40* | decomp. | - | - | - | 50(10)* |
| Na | 759 | 730 | 35.5 | $34.9^+$ | 47 | 1215 | 7.8 | 6.4 | 43.3 | 41(2) |
| K | 538 | 528 | 10.1 | 10.0 | 19 | 1255 | 10 | 8.5 | 10.8 | 7(3) |
| Rb | 480 | 479 | 5.8 | 5.2 | 12 | 1254 | 7 | 5.7 | 12.9 | 7(4) |
| Cs | 568 | 464 | 19.6 | 16.2 | 35 | 1217 | 13.8 | 11.3 | 33.4 | 14(1) |

*estimated from DTA measurements: ± 15% e.s.d. for enthalpies

$$^{+}\Delta H_c\downarrow = \Delta H_c\uparrow + \int_{T_{c\downarrow}}^{T_{c\uparrow}} c_p dT \text{ is valid.}$$



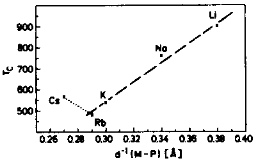


Fig. 3. Transition temperature as function of the inverse metal to phosphorus distance which is proportional to the binding energy $\Delta E_b$.

Fig. 2. Specific heats of the $M_3P_7$ compound near the phase transitions (——). The broken line shows the heat capacity of the high temperature phase (----).
Insert: Lattice heat capacity of $Na_3P_7$ (---), $K_3P_7$ (—), $Rb_3P_7$ (••••) and $Cs_3P_7$ (- ••• -)

of our experimental data below 250K into two sets of $c_p$ curves can be explained (i) as a result of the variation of the molar masses: $Na_3P_7$ : $K_3P_7$ : $Rb_3P_7$ : $Cs_3P_7$ = 0.87 : 1 : 1.43 : 1.83 and consequently the strongest change occurs between $K_3P_7$ and $Rb_3P_7$, being about 43%, and (ii) by the differences in crystalline structure (LT), which is identical for $Rb_3P_7$ and $Cs_3P_7$, but different for $Na_3P_7$. We suggest that $Na_3P_7$ and $K_3P_7$ may have a similar (LT) structure. On the other hand the common high temperature plastic crystalline phase of all compounds is well illustrated in fig.2 by the broken line, which represents the general temperature dependence of $c_p$ in the HT phase in contrast to the LT cryst. modifications, although the $T_c$ values of the individual compounds are very different.

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