JOURNAL OF MATERIALS SCIENCE 24 (1989) 3380–3386

Heat capacity and Na^+ ion disorder in Nasicon-type solid electrolytes $Na_3M_2P_3O_{12}$ (M_2 = Fe_2, Cr_2, ZrMg) in the temperature range 10 to 300 K

L. ABELLO, K. CHHOR*, M. BARJ, C. POMMIER*
*Laboratoire de Chimie Physique du Solide, and *UA no. 453 CNRS, Université Paris XIII, 93430 Villetaneuse, France*

C. DELMAS
Laboratoire de Chimie du Solide du CNRS, Université Bordeaux I, 33405 Talence, France

Heat-capacity measurements on Nasicon-type solid electrolytes have been performed by adiabatic calorimetry. The lattice contribution is estimated from the usual model using spectroscopic data and the excess heat capacities are discussed in terms of low-temperature magnetic transitions in iron and chromium derivatives and of Na^+ ion disorder in the three compounds at higher temperatures. The entropy excess at 300 K is related to the relative ionic conductivity and the occupancy factors of Na^+-available sites.

1. Introduction

Superionic conductors have been widely investigated during the last few years for use in energy storage. Nasicon, with the formula $Na_3Zr_2Si_2PO_{12}$, first studied by Hong [1], is known to exhibit an ionic conductivity higher than that of Na^+ β'' alumina above 300° C. It was the starting material for the development of numerous compounds substituting silicon and zirconium by phosphorus and metallic ions (Cr^{3+}, Fe^{3+}, Sc^{3+}, etc.), respectively. Numerous studies, particularly by X-ray diffraction, neutron diffusion, infrared and Raman spectroscopies, have been performed on these compounds in order to understand the high ionic conductivity of some of them related to their composition and structure [2–10].

The Nasicon-type structure in compounds $Na_3M_2P_3O_{12}$ (M = Cr, Fe, . . .) is a three-dimensional lattice of corner sharing PO_4 tetrahedra and MO_6 octahedra (Fig. 1). Two types of site are available for the Na^+ ions in the high-temperature rhombohedral structure: two S_1 and six S_2 sites per primitive cell ($Z = 2$). The monoclinic distortion in the room-temperature phase leads to the splitting of the S_2 sites into two S_2' and four S_2''. Phase transitions at 368, 418 and 348, 411, 439 K have been found in $Na_3Fe_2P_3O_{12}$ and $Na_3Cr_2P_3O_{12}$, respectively, from differential thermal analysis (DTA) experiments [4].

It has been shown that the ionic conductivity in these compounds is related to a partial occupation of S_1 sites and jumps of Na^+ cations from one type of site to another through "bottlenecks" of oxygen atoms [9, 10]. This mechanism could be assisted by rotations of PO_4 tetrahedra leading to an increase in the diffusion windows. Besides their transport properties, some of these compounds (M = Ti, V, Cr, Fe) exhibit magnetic transition at low temperature, as shown from susceptibility measurements [11]. The Néel temperatures reported for chromium and iron derivatives are around 12 and 45 K, respectively. Furthermore, neutron scattering experiments on $Na_3Cr_2P_3O_{12}$ have shown that strong quasielastic and inelastic components associated with the magnetic scattering of Cr^{3+} ions are observed at temperatures as high as 400° C [6, 12].

In a preliminary paper [13], we reported the first heat-capacity measurements between 10 and 310 K on $Na_3ZrMgP_3O_{12}$ and $Na_3Cr_2P_3O_{12}$. Estimated excess configurational entropy at 300 K was interpreted in terms of Na^+ disordered distribution on different available sites in the crystal. Here we report the results of a more complete low-temperature thermodynamic study on both compounds, as well as on the isomorphous iron derivative. The Na^+ disorder entropy in the three solids is estimated and discussed in the light of structural information. Furthermore, the magnetic transitions in the chromium and iron compounds are studied.

2. Experimental details

The compounds studied were prepared from finely ground stoichiometric mixtures of Na_2CO_3, $(NH_4)_2HPO_4$ and metal oxides heated in a gold crucible. Successive decompositions of the ammonium phosphate and sodium carbonate take place around 300 and 600° C, respectively, the reaction temperature with the metal oxides depends on the nature of the metal, around 1000° C with chromium and 900° C with iron [14]. Between each step, the sample is again ground and pressed into pellets.

Heat-capacity measurements were made on a

0022–2461/89 $03.00 + .12

TABLE I Molar heat capacity and thermodynamic functions of $Na_3ZrMgP_3O_{12}$ crystal

T (K)	C_p ($J\,mol^{-1}\,K^{-1}$)	$H(T) - H(0)$ ($J\,mol^{-1}$)	$S(T) - S(0)$ ($J\,mol^{-1}\,K^{-1}$)	$-[G(T) - G(0)]/T$ ($J\,mol^{-1}\,K^{-1}$)
10	0.96	2.4	0.32	0.08
20	7.68	38.4	2.56	0.64
30	24.60	196.5	8.72	2.18
40	42.84	531.5	18.24	4.95
50	62.86	1 059	29.93	8.74
60	83.40	1 790	43.20	13.36
70	103.6	2 726	57.58	18.64
80	122.9	3 860	72.69	24.45
90	141.2	5 181	88.24	30.67
100	158.2	6 679	104.0	37.21
110	174.2	8 342	119.8	44.01
120	189.1	10 160	135.6	50.98
130	203.2	12 120	151.3	58.10
140	216.4	14 220	166.9	65.32
150	228.8	16 450	182.2	72.60
160	239.8	18 790	197.4	79.93
170	251.1	21 244	212.2	87.27
180	262.3	23 811	226.9	94.63
190	273.1	26 489	241.4	102.0
200	283.4	29 270	255.7	109.3
210	293.0	32 150	269.7	116.6
220	301.8	35 130	283.6	123.9
230	309.8	38 190	297.1	131.1
240	317.1	41 320	310.5	138.3
250	323.6	44 530	323.6	145.5
260	329.6	47 790	336.4	152.6
270	335.1	51 120	348.9	159.6
280	340.4	54 500	361.2	166.6
290	346.0	57 930	373.3	173.5
300	352.0	61 420	385.1	180.4
310	359.1	64 970	396.7	187.1

laboratory-made automated adiabatic calorimeter described elsewhere [15]. The sample brass cell with 7 cm^3 internal volume was filled with 19.559 g $Na_3Fe_2P_3O_{12}$ or 16.738 g $Na_3ZrMgP_3O_{12}$ powder. The available amount of the chromium compound was only 8.063 g. The cell has a re-entrant well containing the sample heater and two germanium and platinum sensors for temperature measurements below and above 30 K, respectively. The precision of the heat-capacity measurements is lower than 0.5% between 100 and 300 K, increases to 1% at 40 K and is estimated to be around 5% below 20 K.

Raman spectra were recorded using a Coderg T800 triple monochromator spectrophotometer equipped with an argon laser.

3. Results and discussion

3.1. Experimental results

More than 300 experimental heat-capacity measurements were performed on each compound studied between 10 and 310 K. The fitted values, as well as the thermodynamic functions, are reported in Tables I, II and III at selected temperatures. The experimental heat-capacity curves are shown in Figs 2, 3 and 4. No anomaly is observed in the case of $Na_3ZrMgP_3O_{12}$ whereas the magnetic transitions in iron and chromium derivatives appear as a peak with maximum C_p values at 46 and ~ 10 K, respectively. These temperatures are in good agreement with the results of magnetic susceptibility measurements [11].

Anomalous features were observed when studying the chromium compound $Na_3Cr_2P_3O_{12}$. The C_p values obtained at temperatures below about 150 K were very dependent on the thermal history of the sample. When it was previously cooled into liquid nitrogen, the measured heat capacities were always higher than those obtained after cooling in liquid helium. Furthermore, in the latter case, spontaneous exothermal effects upon the thermal excitation were observed, leading to absurd C_p values. This is characteristic of a metastable disorder persisting at low temperature. Annealing treatments were performed around 80 K in order to approach the thermodynamically stable phase. These phenomena were not observed on the other two compounds investigated.

No heat-capacity data were previously available in the literature on these compounds, only some derivatives with defined stoichiometry in Nasicon solid solution $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($x = 0, 1, 2, 3$) were investigated [16, 17]. The C_p values estimated from the reported curves for $Na_3Zr_2Si_2PO_{12}$ are around 355 and 395 $J\,K^{-1}\,mol^{-1}$ in [16] and [17], respectively. The first is in better accordance with those obtained in the present work on $Na_3M_2P_3O_{12}$.

3.2. Lattice heat capacity

In order to study the excess entropy at 300 K arising from the Na^+ ion disorder on the available sites of the Nasicon structure, as well as to define precisely the magnetic transition in the chromium and iron derivatives, it is necessary to estimate the lattice heat capacity in the absence of any configurational effects.

The molar lattice heat capacities, C_v, have been calculated using the lattice model previously reported

TABLE II Molar heat capacity and thermodynamic functions of $Na_3Cr_2P_3O_{12}$ crystal

T (K)	C_p ($J\,mol^{-1}\,K^{-1}$)	$H(T) - H(0)$ ($J\,mol^{-1}$)	$S(T) - S(0)$ ($J\,mol^{-1}\,K^{-1}$)	$-[G(T) - G(0)]/T$ ($J\,mol^{-1}\,K^{-1}$)
10	10.20	48.0	4.62	0.18
15	7.80	87.2	7.61	1.80
20	13.87	134.3	10.34	3.62
30	21.94	314.7	17.55	7.05
40	33.59	587.0	25.30	10.63
50	50.57	1 005	34.55	14.46
60	69.26	1 604	45.42	18.69
70	85.80	2 373	57.25	23.34
80	102.9	3 317	69.83	28.36
90	119.4	4 429	82.90	33.69
100	135.6	5 704	96.32	39.28
110	151.7	7 140	110.0	45.08
120	167.8	8 738	123.9	51.07
130	183.5	10 490	138.0	57.21
140	198.4	12 410	152.1	63.48
150	212.1	14 460	166.3	69.86
160	224.2	16 640	180.3	76.33
170	235.2	18 940	194.3	82.86
180	246.2	21 350	208.0	89.43
190	257.6	23 870	221.6	99.03
200	267.2	26 490	235.1	102.6
210	273.4	29 200	248.3	109.3
220	284.8	32 000	261.4	115.9
230	294.0	34 900	274.2	122.5
240	302.9	37 880	286.9	129.1
250	311.3	40 950	299.5	135.6
260	319.2	44 110	311.8	142.2
270	326.5	47 330	324.0	148.7
280	333.6	50 640	336.0	155.2
290	340.7	54 010	347.8	161.6
300	348.1	57 450	359.5	168.0
310	356.1	60 970	371.1	174.4

TABLE III Molar heat capacity and thermodynamic functions of $Na_3Fe_2P_3O_{12}$ crystal

T (K)	C_p ($J\,mol^{-1}\,K^{-1}$)	$H(T) - H(0)$ ($J\,mol^{-1}$)	$S(T) - S(0)$ ($J\,mol^{-1}\,K^{-1}$)	$-[G(T) - G(0)]/T$ ($J\,mol^{-1}\,K^{-1}$)
10	4.21	8.69	1.09	0.22
20	16.12	108.8	7.56	2.12
30	34.06	352.5	17.20	5.45
40	58.81	811.2	30.23	9.95
45	82.50	1 150	38.19	12.63
50	63.83	1 514	45.92	15.64
60	77.91	2 209	58.54	21.72
70	98.58	3 092	72.11	27.94
80	118.6	4 179	86.59	34.36
90	137.9	5 466	101.7	41.00
100	155.3	6 933	117.2	47.84
110	171.6	8 569	132.7	54.85
120	186.9	10 360	148.3	62.00
130	201.1	12 300	163.9	69.23
140	214.5	14 380	179.3	76.54
150	227.0	16 590	194.5	83.90
160	238.8	18 920	209.6	91.28
170	249.9	21 360	224.3	98.68
180	260.4	23 910	238.9	106.1
190	270.4	26 570	253.3	113.4
200	279.9	29 320	267.4	120.8
210	289.0	32 170	281.3	128.1
220	297.7	35 100	294.9	135.4
230	305.9	38 120	308.3	142.6
240	313.9	41 220	321.5	149.8
250	321.4	44 390	334.5	156.9
260	328.6	47 640	347.2	164.0
270	335.5	50 960	359.7	171.0
280	342.0	54 350	372.1	178.0
290	348.3	57 800	384.2	184.9
300	354.4	61 320	396.1	191.7

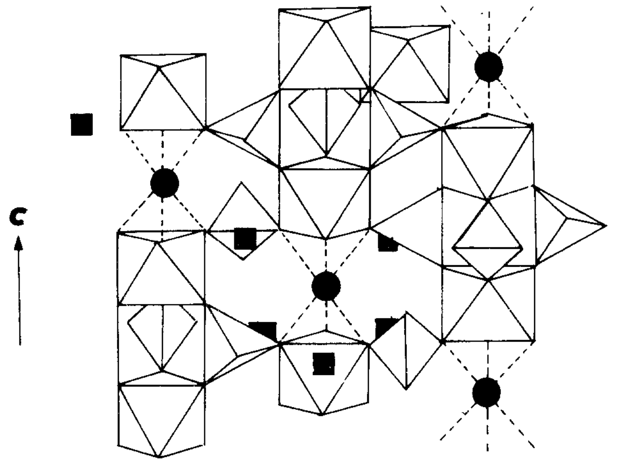

Figure 1 Schematic view of the Nasicon-type structure in $Na_3M_2P_3O_{12}$ crystals. (●) Na (1); (■) Na (2).

in our preliminary paper on chromium and ZrMg compounds [13]. The internal and vibrational modes of PO_4 groups, corresponding to 36 degrees of freedom, were treated as Einstein oscillators. The contribution of translational modes was estimated from two Debye functions associated with phosphate and metallic ion motions (Debye temperature θ_{D1}) and those of the Na^+ cations (Debye temperature θ_{D2}). The vibrational frequencies introduced in the Einstein functions were mean values taken from the experimental Raman spectra [12]. The Debye temperatures were introduced as fit parameters. It was shown that whatever the two θ_D values which give a reasonable fit of the experimental curve in the low-temperature range (namely between 10 and 80 K), little influence on the estimated excess entropy in $Na_3ZrMgP_3O_{12}$ at 300 K was observed. All parameters used in this model are reported in Table IV. It should be noticed that the θ_D values for the chromium compound differ slightly from those used in our preliminary communication [13] as far as, in the present case, the stable phase is considered. Furthermore, the Debye temperatures, θ_{D1}, for the three compounds are in accordance with the order of the metallic ion atomic weights.

TABLE IV Parameters used in lattice heat-capacity calculation:

$$C_v^l = 3R \sum_i g_i \frac{x_i^2 e^{x_i}}{(e^{x_i} - 1)^2} + 9R \sum_{j=1}^{2} N_j \left(\frac{T}{\theta_{Dj}}\right)^3 \int_0^{\theta_{Dj}/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

		$Na_3ZrMgP_3O_{12}$	$Na_3Cr_2P_3O_{12}$	$Na_3Fe_2P_3O_{12}$
Einstein functions, $x_i = h\ v_i/kT$, v_i (cm^{-1})				
v_1	$(g_1 = 1)$	1150	1150	1120
v_2	$(g_2 = 2)$	450	430	420
v_3	$(g_3 = 3)$	1150	1150	1120
v_4	$(g_4 = 3)$	600	600	550
v_{rot}	$(g_{rot} = 3)$	280	200	187
Debye functions, θ_{Di} (K)				
θ_{D1}	$(N_1 = 5)$	370	455	387
θ_{D2}	$(N_2 = 3)$	185	200	187

In this approach we have neglected the high-temperature magnetic contribution and that arising from anharmonic vibrations. Consequently, the heat capacities at constant volume (C_v) and constant pressure (C_p) have been confused.

The lattice contribution compared with the experimental heat capacity, $C_{p,m}$, is shown for each compound in Figs 2 to 4. In the common range of the curves, the fits are within 1% for ZrMg and iron derivatives but about 2% for the chromium compound. As stated above, for the latter compound, the existence of a small residual amount of metastable phase is possible and this leads to some discrepancies in the C_p measurements. Excess heat capacities which appear above about 180 K for chromium and iron derivatives and about 120 K for $Na_3ZrMgP_3O_{12}$ are attributed to a configurational contribution arising from Na^+ ion disorder. The molar excess entropies (S_{ex}) are shown in Fig. 5, for the three compounds. At 300 K, S_{ex} is estimated to be 2.3, 2.8 and 6.7 J K^{-1} mol^{-1} for iron, chromium and ZrMg derivatives, respectively.

3.3. Magnetic transition in $Na_3Cr_2P_3O_{12}$ and $Na_3Fe_2P_3O_{12}$

There have been some investigations of the magnetic properties of these compounds. Susceptibility measurements show characteristic minima on the $\chi^{-1} = f(T)$ curves associated with antiferromagnetic

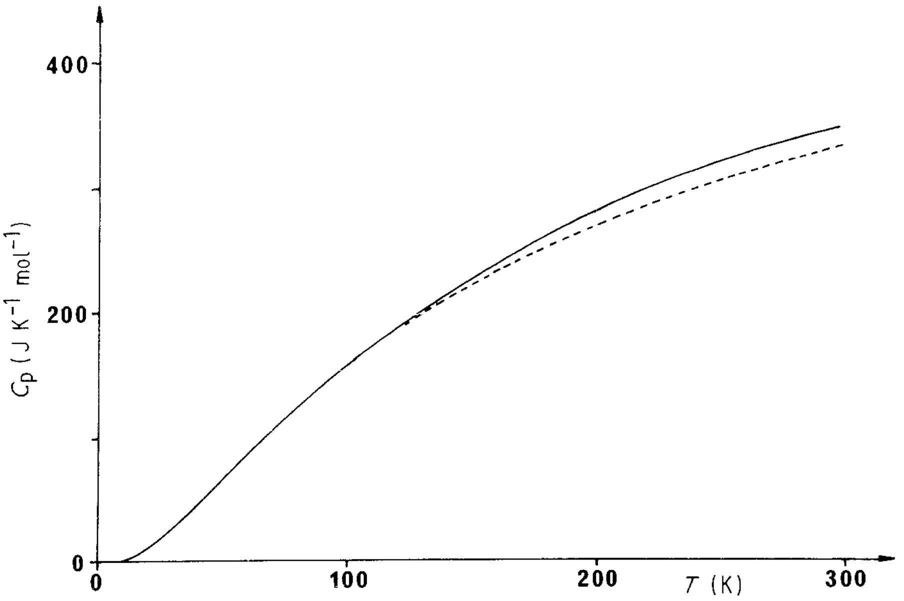

Figure 2 Heat capacity of $Na_3ZrMgP_3O_{12}$: (——) experimental curve, (- - -) estimated lattice heat capacity.

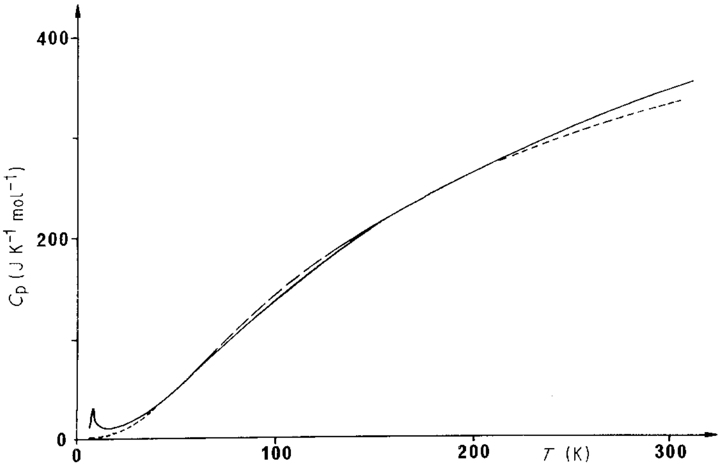

Figure 3 Heat capacity of $Na_3Cr_2P_3O_{12}$: experimental curves (——) without and (— —) with residual disorder; (- - -) estimated lattice heat capacity.

ordering at low temperature [11]. The given temperatures for these minima are around 47 and 12 K for iron and chromium derivatives, respectively. The iron paramagnetic Curie temperature, θ_p, is distinctly negative and indicates the dominance of antiferromagnetic interactions between nearest neighbouring Fe^{3+} ions. However, these couplings must be weak in $Na_3Fe_2P_3O_{12}$ insofar as the atomic Fe–Fe distances are relatively large (~ 0.45 nm). When the M^{3+} spin number decreases, the minimum χ^{-1} values and $|\theta_p|$ decrease, associated with weaker magnetic interactions. Mössbauer spectroscopy on the iron derivative reveals the existence of two different octahedral Fe^{3+} sites at low temperature; however, this non-equivalence vanishes in the high-temperature phase [18]. Neutron scattering experiments have been performed on $Na_3Cr_2P_3O_{12}$. The inelastic component observed around 16 cm^{-1} was tentatively interpreted in terms of Cr–Cr pairs allowed electronic transition between $|SM\rangle$ levels [13]. These excitations are absent in the low frequency spectrum of the non-magnetic ZrMg derivative.

The heat-capacity anomalies observed in the $Na_3Cr_2P_3O_{12}$ and $Na_3Fe_2P_3O_{12}$ C_p curves (Figs 3 and 4) are obviously associated with the antiferromagnetic ordering process. The theoretical entropy increase going from a completely ordered spin state to a completely disordered one is equal to $R \ln (2S + 1)$. An estimation of the experimental S_{mag} and comparison with the theoretical value can be made provided that the magnetic contribution to overall heat capacity can be separated. The usual methods adopted by various authors for this separation have been either to estimate the lattice heat capacity of the magnetic material combining Debye and Einstein functions or to apply the so-called "corresponding state" method [19] by scaling the measured heat capacities from those of a non-magnetic isomorphous substance. Among the three compounds studied only the ZrMg derivative is diamagnetic but it is not a very good reference for the estimation of the normal heat capacity of chromium and iron derivatives insofar as the occupation factors of Na^+ ions in these crystals are different at a given temperature (this point will be discussed in the next section). So, the lattice heat capacities calculated in Section 3.2 have been used to derive magnetic thermodynamic quantities.

For $Na_3Cr_2P_3O_{12}$, the lack of experimental C_p values below 10 K prevents us from determining the entropy variation associated with the magnetic ordering process. Therefore, the following discussion is restricted to the iron compound. The experimental heat capacity

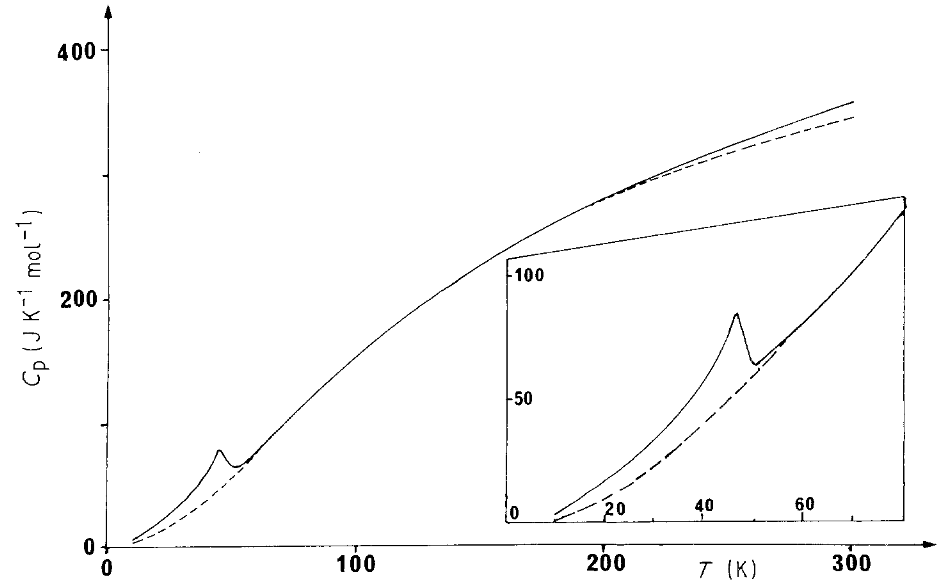

Figure 4 Heat capacity of $Na_3Fe_2P_3O_{12}$:(——) experimental curve, (- - -) estimated lattice heat capacity.

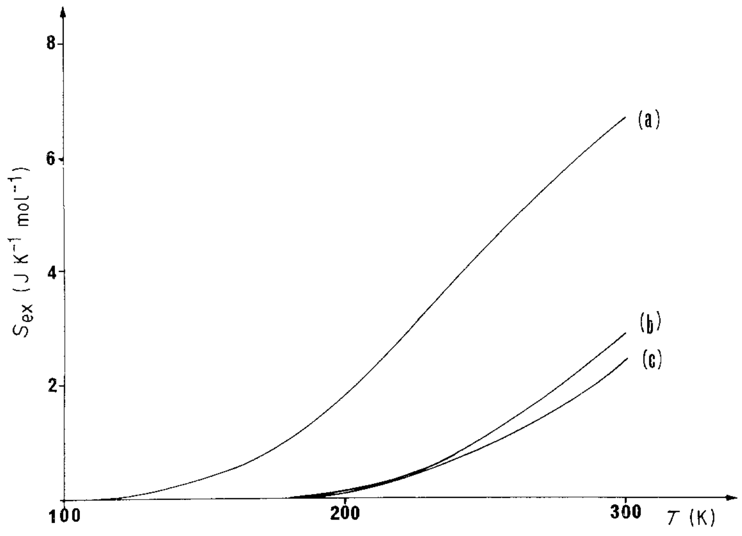

Figure 5 Molar excess entropy arising from Na^+ ion disorder in (a) $Na_3ZrMgP_3O_{12}$; (b) $Na_3Cr_2P_3O_{12}$; (c) $Na_3Fe_2P_3O_{12}$.

and the lattice contribution in the magnetic transition range, below about 80 K are shown in Fig. 4. Integration of the excess heat capacity in this range leads to the transition enthalpy and entropy: $\Delta H_{\mathrm{magn}} = 480\,\mathrm{J\,mol^{-1}}$, $\Delta S_{\mathrm{magn}} = 15.8\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

The evolution of S_{magn} against temperature is shown in Fig. 6. The existence of some discrepancy between the expected ($R \ln 6 = 14.9\,\mathrm{J\,K^{-1}\,mol^{-1}}$) and the limited experimental values cannot be considered surprising, in view of the crudeness of the lattice approximation and extrapolation of experimental heat capacity below 10 K. However, the magnetic entropy obtained in the present case can be considered as evidence for the expected spin order–disorder transition in $Na_3Fe_2P_3O_{12}$.

3.4. Na^+ disorder in Nasicon compounds

As mentioned above, the Na^+ ion mobility in the Nasicon structure of $Na_3M_2P_3O_{12}$ compounds induces important disorder associated with the observation of large Raman bands at room temperature. From the thermodynamic point of view, two phenomena contribute to the entropy increase: the disorder related with the occupation factors, p_i, of the various kinds of available sites, and the occurrence of several distinct possible configurations of the Na^+ ions for a given set of p_i. Fig. 6 schematically shows possible Na^+ distributions in a unit cell. Each of them, which is characterized by the numbers of Na^+ ions n_1, n_2', n_2'' on S_1, S_2' and S_2'' sites respectively, has a probability factor, τ_i, at temperature T and corresponds to $[N_i]$ distinguishable possible configurations. At a given temperature, T, the molar excess entropy would then be

$$S_{\mathrm{exc}} = -\frac{R}{Z}\sum_i \tau_i \ln(\tau_i/N_i)$$

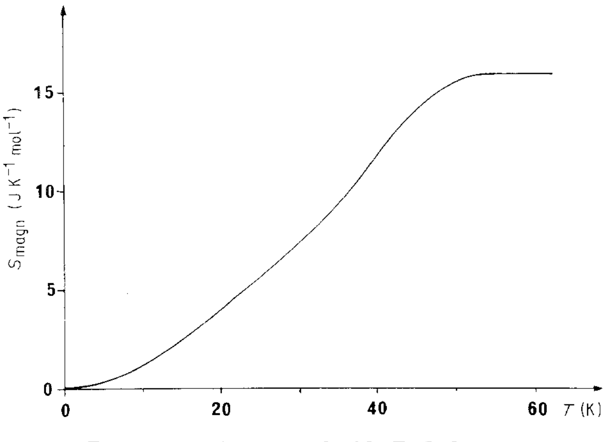

Figure 6 Excess magnetic entropy for $Na_3Fe_2P_3O_{12}$.

The probability factors of the various distributions and the occupation factors (p_1, p_2', p_2'') of the three types of site are related through balance equations for Na^+ ions presented in [13].

Potential energy calculations performed on the rhombohedral structure of $Na_3Cr_2P_3O_{12}$ have shown that the symmetrical cation arrangements with fully occupied sites 1 (symmetrical 2/2/2 or 2/0/4 distributions, Fig. 7) have the lowest energy while that with empty sites 1 (0/2/4 distribution) is energetically unfavoured [10]. At very low temperatures, we assumed that a completely ordered ($p_1 = 1$, $p_2' = 0$, $p_2'' = 1$) with a square planar Na^+ ion arrangement would be the stable one (2/0/4 in Fig. 7). As the temperature is raised, other distributions are allowed and, for chromium and iron derivatives, the population factors have been estimated at 300 K from X-ray [5] and neutron diffraction studies [6].

For $Na_3Fe_2P_3O_{12}$, the values $p_1 = 1$, $p_2' = p_2'' = 0.66$ were reported. Ionic conductivity measurements [20] are also in accordance with a rather low disorder at this temperature. The system of Na^+ ion balance equations can be solved with $\alpha_1 = 2/3$, $\alpha'' = 1/3$ and all other probability factors (Fig. 7) being equal to zero, that is the crystal would be a random mixture of two cells with 2/2/2 symmetrical configurations and one cell with 2/0/4 distribution. The corresponding minimum disorder excess entropy would then be $2.6\,\mathrm{J\,K^{-1}\,mol^{-1}}$ (or $4.6\,\mathrm{J\,K^{-1}\,mol^{-1}}$ considering the two distinguishable symmetrical 2/2/2 distributions to be equally populated). From our heat-capacity measurements and estimated lattice contribution, the calculated entropy excess at 300 K is $2.3\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

Looking at $Na_3Cr_2P_3O_{12}$ at the same temperature, the ionic conductivity is of the same order of magnitude to that of the iron derivative [20]. The reported occupation factors are $p_1 = p_2' = 0.83$ and $p_2'' = 0.66$. Therefore, the nature of the disorder appears

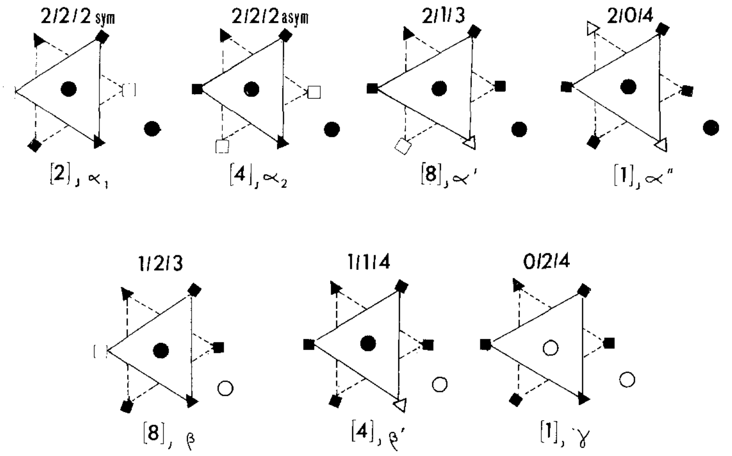

Figure 7 Possible Na^+ ion distributions in $Na_3M_2P_3O_{12}$ unit cell ($[N_i]$, τ_i are the number of distinguishable configurations and the probability factor of distribution i). (●, ○) occupied and empty S_1 site, (▲, △) occupied and empty S_2' site, (■, □) occupied and empty S_2'' site.

somewhat different than in the iron compound. The derived distribution in best agreement with these considerations is $\alpha_1 = 2/3$, $\beta' = 1/3$ and all other probability factors equal to zero. The solid would then be described as a mixture of two 2/2/2 symmetrical cells and one 1/1/4 cell. The experimental entropy excess at 300 K, 2.8 J K^{-1} mol^{-1}, is slightly lower than the minimum calculated value (4.6 J K^{-1} mol^{-1}) assuming only one symmetrical 2/2/2 configuration occupied. This could mean a non-random mixture of the two types of cell in the crystal. Although the disordering process in iron and chromium compounds occurs above the same temperature range, about 180 K (Fig. 5), it appears different in nature in $Na_3Cr_2P_3O_{12}$ and this could be related to the peculiar thermal behaviour observed in this compound, particularly its ability to remain in the metastable disordered state on cooling below room temperature, as observed during heat-capacity measurements.

No Na^+ site occupation factors are available for $Na_3ZrMgP_3O_{12}$. However, its ionic conductivity at 300 K is about two orders of magnitude larger than that of the other two compounds [20]. We observed that the disordering process began at lower temperatures, above around 100 K and that the calculated entropy excess at 300 K is more than twice the previous ones: 6.7 J K^{-1} mol^{-1} (Fig. 5).

References

1. H. Y. HONG, *Mater. Res. Bull.* **11** (1976) 173.
2. F. d'YVOIRE, M. PINTARD-SCREPEL and E. BRETEY, *C. R. Acad. Sci.* **290C** (1980) 185.
3. C. DELMAS, R. OLAZCUAGA, G. LE FLEM, P. HAGENMULLER, F. CHERKAOUI and R. BROCHU, *Mater. Res. Bull.* **16** (1981) 285.
4. F. d'YVOIRE, M. PINTARD-SCREPEL, E. BRETEY and M. de la ROCHERE, *Solid State Ionics* **9/10** (1983) 851.
5. M. de la ROCHERE, F. d'YVOIRE, G. COLLIN and R. COMES, *ibid.* **9/10** (1983) 825.
6. G. LUCAZEAU, M. BARJ, J. L. SOUBEYROUX, A. J. DIANOUX and C. DELMAS, *ibid.* **18/19** (1986) 959.
7. M. BARJ, Ph. COLOMBAN and H. PERTHUIS, *ibid.* **11** (1983) 157.
8. M. BARJ and Ph. COLOMBAN, *ibid.* **9/10** (1983) 845.
9. H. KOHLER and H. SCHULZ, *ibid.* **9/10** (1983) 795.
10. J. F. BOCQUET, M. BARJ, G. MARIOTTO and G. LUCAZEAU, *ibid.* **28/30** (1988) 411.
11. D. BELTRAN PORTER, R. OLAZCUAGA, C. DELMAS, F. CHERKAOUI, R. BROCHU and G. LE GLEM, *Rev. Chim. Min.* **17** (1980) 458.
12. M. BARJ, Thesis, Paris XIII University (1987).
13. M. BARJ, K. CHHOR, L. ABELLO, C. POMMIER and G. DELMAS, *Solid State Ionics* **28/30** (1988) 432.
14. F. CHERKAOUI, Thesis, Bordeaux, France (1985).
15. K. CHHOR, J. F. BOCQUET and C. POMMIER, *J. Chem. Thermodynam.* **17** (1985) 379.
16. J. MAIER, U. WARHUS and E. GMELIN, *Solid State Ionics* **18/19** (1986) 969.
17. V. VON ALPEN, M. F. BELL and W. WICKELHAUS, *Mater. Res. Bull.* **14** (1979) 1317.
18. D. BELTRAN-PORTER, R. OLAZCUAGA, L. FOURNES, F. MENIL and G. LE FLEM, *Rev. Phys. Appl.* **15** (1980) 55.
19. J. W. STOUT and E. J. CATALANO, *J. Chem. Phys.* **23** (1955) 2013.
20. A. FELTZ and S. BARTH, *Solid State Ionics* **9/10** (1983) 817.

Received 22 July
and accepted 22 November 1988