

NEUTRON SCATTERING AND DIFFRACTION STUDY OF $\text{Na}_3\text{Cr}_2\text{P}_3\text{O}_{12}$, $\text{NaZr}_2\text{P}_3\text{O}_{12}$ AND $\text{Na}_3\text{ZrMgP}_3\text{O}_{12}$

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A polycrystalline sample of $\text{Na}_3\text{Cr}_2\text{P}_3\text{O}_{12}$ has been studied by Quasielastic and Inelastic Neutron Scattering in the 303-673 K temperature range. For $Q \leq 0.5 \text{ \AA}^{-1}$ a strong quasielastic contribution is observed. It has a lorentzian shape and its width varies as DQ^2 . It has been interpreted in terms of magnetic scattering. Above $Q = 1 \text{ \AA}^{-1}$ it gives rise to a broad signal which can be considered as a flat background as regards to the IN6 resolution ($\sim 130 \text{ \mu eV}$), while a narrow component develops ; this component has been fitted with a model of Na jumps. No quasielastic scattering has been observed for $\text{NaZr}_2\text{P}_3\text{O}_{12}$ and $\text{Na}_3\text{ZrMgP}_3\text{O}_{12}$. Inelastic spectra for the three compounds have been recorded up to 600 cm^{-1} and discussed in terms of vibrational amplitudes. The structure of $\text{Na}_3\text{Cr}_2\text{P}_3\text{O}_{12}$ at 573 K has been studied by neutron diffraction.

1. INTRODUCTION

The compounds investigated here belong to the Nasicon family. Their frame is made of MO_4 tetrahedra ($M = \text{Si}$ and P) sharing corners with $\text{M}'\text{O}_6$ octahedra ($M' = \text{Mg}$, Cr , Fe , Zr). For $\text{Na}_3\text{Cr}_2\text{P}_3\text{O}_{12}$, the sodium ions are distributed among two main types of sites labelled $^1, 2 \text{ Na}_1$ and Na_2 (Fig. 1). The temperature dependence of the occupation factors of these sites (for Na_1 , $f = 0.83$ and 0.74 at 298 and 453 K respectively) along with the observation of an ionic conductivity $^3, 4$ of about $5 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$ at 400°C is an indication of Na^+ mobility. For $\text{NaZr}_2\text{P}_3\text{O}_{12}$, only the Na_1 sites are occupied at 300 K ⁵ and its conductivity is 500 times smaller at 400°C than that of $\text{Na}_3\text{Cr}_2\text{P}_3\text{O}_{12}$, while the conductivity of $\text{Na}_3\text{MgZrP}_3\text{O}_{12}$ is only 5 times smaller than that of the chromium derivative. In other terms the partial filling of Na_2 sites is determinant for increasing the Na^+ mobility⁶.

The aim of this work is to determine the dynamics of Na^+ ions : residence time, activation energy, geometry of the motion, jump mechanism

(single ions or correlated motions). The diffusion path can be guessed easily : a Na^+ ion sitting in Na_1 site can reach a vacant Na_2 site by proceeding in straightline to the bottleneck BN_1 (in the middle of the $\text{O}_1\text{O}_2\text{O}_3$ triangle), then passing at the Na_3 position and again through a second bottleneck BN_2 (nearly equidistant from Na_3 ^{7, 10} (Fig. 1).

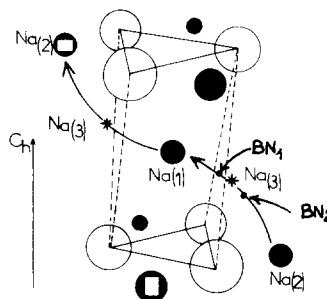


FIGURE 1
Conducting path for Na^+
 BN_i : bottlenecks
 $\text{Na}(i)$: Na^+ positions.

Far infrared measurements in $MZr_2P_3O_{12}$ ($M = Na, K, Ag$) have allowed to assign the 85 cm^{-1} band to the cation oscillations in the Na_1 site⁸. Making the usual approximations⁹, one derives a potential barrier of 31 Kcal.mol^{-1} for a period $d = 6.6\text{ Å}$. For $Na_3Cr_2P_3O_{12}$, both IR bands at 58 and 88 cm^{-1} can be assigned to Na_2 and Na_1 sites respectively, in that case assuming a pseudo period of 3.3 Å one derives potential barriers of 3.6 and 8.3 Kcal.mol^{-1} respectively. Potential calculations are also in progress¹⁰.

Preliminary measurements⁶ had shown that a strong Quasi-Elastic Neutron Scattering (QENS) was observed; it was suggested that for small Q 's, the quasi-elastic scattering was due to magnetic scattering of Cr^{3+} ions, while for Q larger than 1 Å^{-1} the quasi-elastic scattering could be due to Na motions.

In order to eliminate the presence of magnetic scattering, we have prepared $Na_3MgZrP_3O_{12}$ and in order to play on the mobility of Na^+ we have also studied $NaZr_2P_3O_{12}$ for which the mobility of Na^+ is expected to be strongly reduced. Moreover for increasing the jump rates of Na^+ in our compounds we have extended our measurements up to 300°C and 400°C .

Actually the scattering law $S(Q, W)$ associated with Na^+ motions is written by using a model of jumps between definite sites either restricted to a unit cell or extending to the whole crystal (e.g. such as in the Chudley-Elliott model¹²). Thus the mean atomic positions along with the occupation factors at the same temperatures as for QENS are very helpful; in particular for $Na_3Cr_2P_3O_{12}$ which exhibits three phase transitions

$\alpha - 75^\circ\text{C} - \alpha' - 138^\circ\text{C} - \beta - 166^\circ\text{C} - \gamma$,

(below 138°C , it is monoclinic, above 138°C it is trigonal). Thus we have studied the static structure of $Na_3Cr_2P_3O_{12}$ at 300°C by undertaking neutron diffraction measurements. Finally the presence of a magnetic ordering was also

investigated, specially at low temperature, where an antiferromagnetic behaviour has been observed¹³. The diffraction results will be analyzed in a first part, the quasi-elastic spectra and the inelastic spectra will be discussed in second and third parts.

2. EXPERIMENTAL

2.1. Neutron Diffraction on $Na_3Cr_2P_3O_{12}$

Diffraction experiments have been performed at the Institut Laue Langevin (Grenoble). The temperature range $300-575\text{ K}$ was investigated on the D1A diffractometer using an incident wavelength of 1.909 Å with a 2θ range comprised between 6 and 120 degrees.

The low temperature measurements ($2-80\text{ K}$) were performed on the D1B instrument using the incident wavelength of 2.52 Å for a 2θ range of 80 degrees.

The experimental Neutron patterns were analyzed according to the RIETVELD profile data fit method.

2.2. Neutron Scattering

The three compounds have been studied at 300°C on the IN6 time of flight spectrometer at ILL, using wavelengths of 5.1 Å and 5.9 Å . The corresponding mean resolutions are of 130 and 90 μeV respectively. In addition we have also studied $Na_3Cr_2P_3O_{12}$ at 30°C , 150°C and 400°C . The polycrystalline samples were placed in aluminium flat containers and maintained at 300°C for ten hours before scattering measurements in order to eliminate any trace of moisture. A 90% transmission was achieved. Eighteen angles were analyzed, Bragg peaks were eliminated. The data were corrected from absorption and self shielding.

3. DIFFRACTION RESULTS

3.1 High temperatures

The results are summarized in Table 1, figures 2.a and 2.b present the diagrams used for the profile refinements along with observed and calculated patterns.

The monoclinic α -phase at 300 K has been described² by the $C_{2/c}$ space group ($Z = 12$), the last refinement cycle containing 120 adjustable parameters.

In order to reduce the number of the parameters (21 in our last refinement cycle) and for comparing directly both structures at 300K and 575K, we have described the α -phase in the $R\bar{3}c$ space group normally used for describing the rhombohedral high temperature γ -phase², consequently the diffraction patterns shown in figure 2a exhibits superstructure lines.

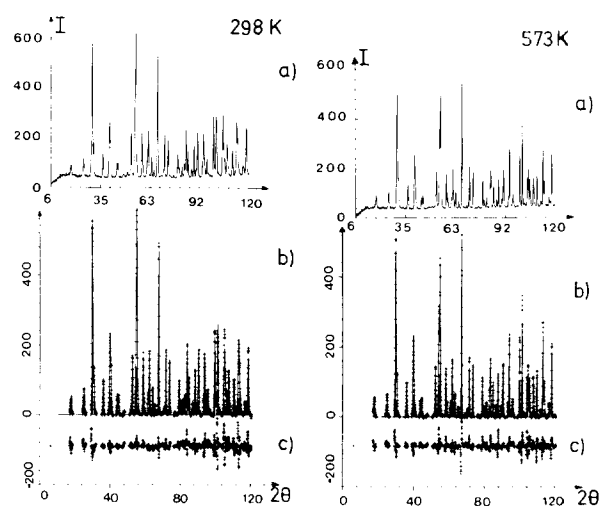


FIGURE 2

Neutron diffraction patterns of $Na_3Cr_2P_3O_{12}$

(a) : experimental data, (b) : calculated
(c) : difference diagram.

However, the most intense of the superstructure lines represents only 2 % of the intensity of the strongest lines of those associated with the average trigonal structure.

Atomic positions and isotropic temperature factors were refined for all the atoms. In the $R\bar{3}c$ space group, the chromium, oxygen and phosphorus atoms occupy their usual positions². In addition, for Na_1 and Na_2 sites, the occupation factor and anisotropic temperature factor were refined.

The Na_2 sites are octahedrally distributed around Na_1 sites.

TABLE I
Crystallographic data of $Na_3Cr_2P_3O_{12}$ at various temperatures.

$R\bar{3}c$	T = 300 K	T = 575 K	T = 575 K
a (Å)	8.6476(2)	8.6548(2)	8.6548(2)
c (Å)	21.6169(6)	21.8218(6)	21.8218(6)
Chromium (0, 0, z)			
z	0.1465(4)	0.1474(5)	0.1474(5)
B(A)	0.49 (16)	1.35(19)	1.40(15)
Phosphorus (x, 0, 1/4)			
x	0.2911(5)	0.2879(6)	0.2879(6)
B	0.20(9)	1.00(12)	1.10(10)
Oxygen (x, y, z)			
x	0.1746(5)	0.1725(5)	0.1725(5)
y	-0.0306(5)	-0.0355(5)	-0.0355(5)
z	0.1934(2)	0.1943(2)	0.1943(2)
B(A)	1.77(8)	2.09(8)	2.09(9)
Oxygen (x, y, z)			
x	0.1925(4)	0.1919(4)	0.1919(5)
y	0.1675(5)	0.1664(5)	0.1664(5)
z	0.0899(1)	0.0902(1)	0.0902(1)
B(A)	0.80(7)	1.05(7)	1.10(7)
Sodium Na_1 (0, 0, 0)			
B11 = B22 = 2B12	16.9(2.5)	21.9(2.4)	14.2(2.0)
B33	2.6(0.8)	-8.8(7)	0.9(0.7)
B13 = B23	0.0	0.0	0.0
n	0.79(4)	0.72(5)	0.73(4)
Sodium Na_2 (x, 0, 1/4)			
x	0.6315(14)	0.6275(15)	0.6275(10)
B11	1.9(5)	1.7(4)	2.1(4)
B22 = 2B12	2.6(6)	2.0(6)	2.0(6)
B33	8.7(9)	8.0(7)	8.0(7)
2B23 = 2B13	2.9(6)	-0.3(5)	0.1(3)
n	2.20(4)	2.20(5)	2.20(4)
Sodium Na_3 (x, y, z)			
x			-0.02
y			-0.16
z			-0.04
B(A)			2.0
n			0.07(4)

A third site, denoted Na_3 located at $(-0.02, -0.16, -0.04)$ has been introduced for the refinement at 575 K. This position reported by KOHLER⁷, is located between Na_1 and Na_2 sites. It corresponds to an intermediate position comprised between both "bottlenecks" BN1 and BN2 and could be a metastable position involved in the diffusion process for the Na^+ ions. The corresponding results are given in column 3 (see Table I). Because of the small occupation factor of the Na_3 site, its position has been fixed and its temperature factor was maintained at a small value, the total occupation factor for Na being fixed at 3.0 per formula unit. The corresponding reliability factor (6.3 %) and the standard deviation values confirm the fact that the superstructure lines do not play a determinant role in the refinement.

The calculated parameters for the high temperature phase are listed in column 2. Although the reliability factor is correct (7.4 %), Fourier difference between observed and calculated intensities have been performed without taking into account Na_3 ions because its site occupancy is very low by comparison with the Na concentration calculated at 300 K.

3.2. Low temperatures

Although the variation of the inverse of the magnetic susceptibility (χ^{-1}) vs temperature ¹³ shows a minimum for $T = 12$ K ($\theta_P = -34$ K) we have not observed new Bragg peaks connected with a tridimensional magnetic structure. At 2K, only a weak modulation of the background is observed with a maximum for $d = 6.35 \text{ \AA}^{-1}$. This modulation likely originates from a short range magnetic ordering, however its weak intensity prevents a further analysis.

4. QUASI-ELASTIC SCATTERING (QES)

4.1. Results

Figure 3 presents the Quasi-elastic results for $\text{Na}_3\text{Cr}_2\text{P}_3\text{O}_{12}$ at 400°C . A strong Quasielastic signal is observed between -1.2 and 1.2 meV, it has been fitted with a Lorentzian function (ESFIT6 standard program at ILL), its integrated intensity decreases with Q from 0 to 1 \AA^{-1} and increases from 1 to 2 \AA^{-1} (see Fig.3 in which only 6 angles are reported); its half-width at half maximum (HWHM) is also strongly Q dependent (Fig. 6). One can either consider that there is a unique scattering process presenting a narrowing for $Q \sim 1 \text{ \AA}^{-1}$ or several processes; the first one should follow a DQ^2 law at small Q 's ($Q < 0.4 \text{ \AA}^{-1}$), by extrapolation, for $Q > 1 \text{ \AA}^{-1}$ it should be larger than 500 \mu eV and should give rise to a broad background. This assumption is strengthened by the observation of an unusual strong background which increases from $Q = 0.2 \text{ \AA}^{-1}$ reaches a maximum for $Q \sim 1 \text{ \AA}^{-1}$ and decreases for large Q values (results of ESFIT6).

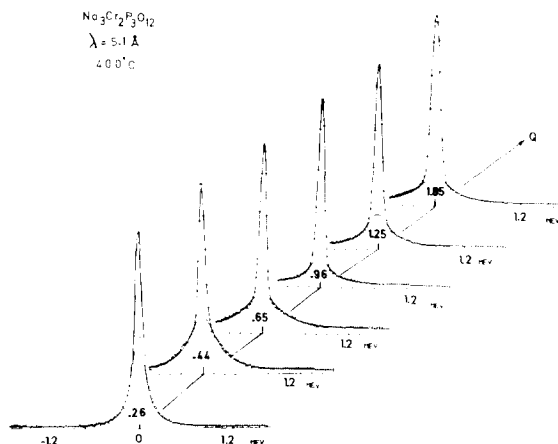


FIGURE 3
Quasi-elastic scattering of $\text{Na}_3\text{Cr}_2\text{P}_3\text{O}_{12}$
at 673 K. Only single angles are reported.

Thus the quasi-elastic component observed for $Q \gg 1 \text{ \AA}^{-1}$ could belong to a second type of scattering. As stated above, its intensity increases with Q but its HWHM remains approximately constant in the 1 - 2 \AA^{-1} Q range and consequently the QE signal between 0.6 and 1 \AA^{-1} must be the superimposition of two components, while for $Q > 1 \text{ \AA}^{-1}$ one has a lorentzian quasi-elastic component plus a flat background. Note that for small Q the background originates from an inelastic feature extending up to 4 meV (Fig. 4b).

The Q dependence of the fraction of the quasi-elastic intensity (noted : 1-EISF) is represented in Fig. 5. This behavior is observed for all the temperatures investigated here. However the HWHM of both components decreases when the temperature is raised from 150 to 400°C (Fig.6).

For $\text{Na}_3\text{ZrMgP}_3\text{O}_{12}$ and $\text{NaZr}_2\text{P}_3\text{O}_{12}$ no quasi-elastic signal is clearly observed.

Figures 4 through 9 can be obtained from the authors in an extended version of this paper along with theoretical background (4.2), discussion of the quasi-elastic (4.3), and inelastic scattering results (5).

6. CONCLUSIONS AND PERSPECTIVES

The QES above $Q \approx 1 \text{ \AA}^{-1}$ is due to magnetic scattering associated with Cr^{3+} ions. It has been discussed and interpreted using De Genne and Lovesey's theories^{14,15}. The relaxation time of the magnetization for $Q \approx 1 \text{ \AA}^{-1}$ and $T = 400^\circ\text{C}$ has been found equal to $2.9 \times 10^{-12} \text{ s}$ while $J \approx 0.6 \text{ cm}^{-1}$ is found much smaller than, for example, RbMnF_3 ²¹.

For $Q \approx 1 \text{ \AA}^{-1}$, the QES is likely due to Na^+ motions. At 400°C it fits nicely the scattering law based on the model of Na jumps between Na_1 and Na_2 sites ($d = 3.5 \text{ \AA}$); the corresponding residence time in Na_1 site is found equal to $\tau_p \approx 4 \times 10^{-12} \text{ s}$, while occupation factor of about 0.75 is in fair agreement with diffraction measurements (see Table I). At 150°C the jump distance is found to decrease towards 1.5 \AA , and the Na_3 site (found in the last refinement of Table I) could be involved in the jump mechanism.

The inelastic frequency distributions for the three compounds have been obtained and compared with the corresponding Raman spectra⁶.

We plan to undertake further experiments to solve some puzzling problems such as the broadening of the QES when the temperature is decreased, both for magnetic and nuclear diffusion.

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