Crystal Data and Spectroscopic Studies of NaNiFe$_2$(AsO$_4$)$_3$

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NaNiFe$_2$(AsO$_4$)$_3$ is the only phase of the NaM^{II}Fe$_2$(AsO$_4$)$_3$ (M^{II} = Mg, Co, Ni, Cu, Zn) that crystallizes as the homologous monoclinic Cr(III) family with space group $P2_{1/c}(C_{2h}^6)$. Its crystallographic parameters were calculated: a = 7.06 Å, b = 9.38 Å, c = 19.63 Å, β = 114.2° (Z = 4). The symmetry sites that Fe(III) occupies and the distortions of the FeO$_6$ polyhedron were analyzed by Mössbauer spectroscopic measures. The IR spectrum of this compound has also been registered and the vibrational modes of the different polyhedra of the lattice have been interpreted. © 1992 Academic Press, Inc.

1. Introduction

In recent years we have studied the crystallographic and spectroscopic properties of certain series of oxoanions such as Li$_3$M^{III}(MoO$_4$)$_3$, M$_3^I$M^{III}(WO$_4$)$_3$, CaM^{III}Sn(PO$_4$)$_3$, and M^{I}M^{II}M$_2^{III}$(AsO$_4$)$_3$ (*1–8*).

Most of these series with Fe(III) or Cr(III) always present analogous structures. However, in the present paper we prove that in arsenates of stoichiometry NaM^{II}M$_2^{III}$(AsO$_4$)$_3$ (M^{III} = Fe or Cr and M^{II} = Mg, Co, Ni, Cu, Zn), a special behavior makes itself evident since NaNiFe$_2$(AsO$_4$)$_3$ is the only phase with Fe(III) maintaining the same monoclinic $P2_{1/c}(C_{2h}^5)$ structure as the correspondent compounds of the homologous family with Cr(III) (*9*).

This special behavior in the NaM^{II}Fe$_2$(AsO$_4$)$_3$ series constitutes an interesting exception to the periodic rules of the crystal-

lographic properties in this type of oxoanion. Thus, it was interesting to estimate the crystallographic data and to investigate their Mössbauer and IR spectroscopic behavior. This study led to obtaining a greater knowledge of the internal vibrations of the polyhedra AsO$_4$, FeO$_6$, and NiO$_6$, to interpreting the couplings of the condensed phase, to establishing correlations between crystallographic and vibrational properties, to determining the characteristics of the site, and to confirming the oxidation state of iron in this lattice.

2. Experimental

Microcrystalline samples of NaNi Fe$_2$(AsO$_4$)$_3$ were obtained by solid state reaction, at 800°C, from stoichiometric Na$_2$CO$_3$, NiO, Fe$_2$O$_3$, and As$_2$O$_5$ mixtures. The fine powdered mixtures were placed in

a platinum crucible and fired in a muffle-turnace at 800°C in several periods totaling 15 hr with intermediate grindings of the reaction mixture. Samples were characterized by chemical analyses and X-ray powder diffractometry.

X-ray powder diagrams (Debye–Scherrer) have been obtained with a Rigaku 2002 Miniflex diffractometer, using Ni-filtered Cu$K\alpha$ radiation (λ = 1.5418 Å) and NaCl and quartz as external calibration standards. Unitary cell parameters have been determined from the corresponding powder diagram by using an ARC 286-AT computer, applying a modified version of the Werner "PIRUM" program (*10*).

Mössbauer spectra were obtained in a constant acceleration mode with transmission geometry and simultaneous accumulation in two halves of 256 channels each of a conventional multiscaler. The spectra were fitted independently with Lorentzian curves on a parabolic baseline with a nonlinear least-squares program with constraints. A ^{57}Co/Rh source of 10 mCi activity was employed. Infrared spectra were recorded by a Perkin–Elmer 683 spectrometer using the KBr pellet technique.

3. Results and Discussion

3.1. Crystallographic Data

The powder diagram (Table I) was registered and was identical to those obtained for such compounds with Cr(III) which crystallize in a monoclinic distorted langbeinite-type structure. The crystallographic parameters obtained from this diagram are shown in Table II. All reflections observed in the diagram satisfy the extinction rules of the space group $P2_{1/c}$(C_{2h}^5, No. 14). Thus, the structural ratio of this unique phase is demonstrated with the correspondent Cr(III) compounds. The other compounds with Fe(III) give different diagrams with another crystalline structure (*11*).

TABLE I

X-Ray Powder Data for NaNiFe$_2$(AsO$_4$)$_3$

$h\,k\,l$	d_o (Å)	d_c (Å)	I/I_o
$\bar{1}\,0\,2$	6.69	6.69	25
$\bar{1}\,1\,1$	5.63	5.64	56
$1\,1\,0$	5.30	5.31	33
$\bar{1}\,1\,4$	4.20	4.19	38
$0\,2\,3$	3.690	3.688	44
$\bar{1}\,2\,4$	3.317	3.315	20
$1\,0\,4$	3.121	3.123	33
$\bar{1}\,1\,6/3\,0\,2$	3.084	3.085	23
$0\,0\,6$	2.983	2.984	23
$1\,2\,3$	2.895	2.899	33
$\bar{2}\,0\,6$	2.847	2.848	98
$\bar{2}\,2\,2$	2.815	2.813	100
$1\,3\,1$	2.704	2.706	51
$2\,2\,0$	2.654	2.655	56
$2\,1\,2$	2.595	2.592	26
$0\,2\,6$	2.519	2.518	41
$\bar{2}\,2\,7$	2.263	2.264	57
$2\,0\,6$	1.844	1.843	23
$0\,3\,8$	1.821	1.820	28

3.2. IR Spectrum

The free arsenate ion (Td symmetry) possesses four internal vibrations: a symmetric stretching vibration, $\nu_1(A_1)$, a symmetric deformation mode, $\nu_2(E)$, an antisymmetric stretching vibration, $\nu_3(F_2)$, and an antisymmetric deformation mode, $\nu_4(F_2)$. Out of these, only the F_2 species are active in IR. The knowledge of the crystallographic data allows interpreting the spectrum through site symmetry analysis. In the lattice, the AsO$_4^{3-}$ ions are located in general C_1 positions. Thus, as shown in Table III, all degenerations are removed and all components show activity in IR. However, also as shown in Table III, different factor group splittings are expected in the crystal lattice.

Figure 1 shows the IR spectrum of this compound in the region of the AsO$_4^{3-}$ internal vibrations, where there also appear the FeO$_6$ internal vibrations and the Ni(II) polyhedra. The assignation for this spectrum is shown in Table IV. Our results coincide

TABLE II

CRYSTAL DATA FOR MONOCLINIC $NaNiFe_2(AsO_4)_3$

System Monoclinic
Space group $P2_{1/c}$
Unit cell parameters α (Å) $=$ 7.06 ± 0.01
                     b (Å) $=$ 9.38 ± 0.01
                     c (Å) $=$ 19.63 ± 0.01
                     β (°) $=$ 114.2 ± 0.1
                     V (A³) $=$ 1186 ± 2
                     $Z =$ 4
Pycnometric density 3.40 ± 0.1 g/cm³
Calculated density 3.42 ± 0.01 g/cm³

FIG. 1. IR spectrum of $NaNiFe_2(AsO_4)_3$.

with the expectations based on site symmetry analysis. Unfortunately, a good Raman spectrum could not be attained for this dark-brown color compound and the assignation of the symmetric modes in IR has been carried out taking into account one of our previous works (8).

In the region of the stretchings, we have assigned the 860-cm⁻¹ band to the vibration of the symmetric stretching. This mode is inserted among the three ν_3 components as it happens in other similar arsenates (12). The splittings observed prove that the AsO_4^{3-} groups are little distorted in the monoclinic lattice.

In the deformation region, 350–590 cm⁻¹, under the influence of the site group and of the factor group, both ν_2 and ν_4 are split into components, some of which may be strongly mixed up (13). But for relative intensities,

the three bands at 496, 474, and 447 cm⁻¹ and the two bands at lower frequencies in 394 and 390 cm⁻¹ are considered essentially components of ν_4 and ν_2, respectively. It is also probable that some of the last bands assigned to the deformation modes are coupled with vibrational modes of the Ni–O bond and the lattice modes.

TABLE III

CORRELATION BETWEEN THE POINT GROUP T_d, THE SITE GROUP C_1, AND THE FACTOR GROUP C_{2h}

T_d		C_1	C_{2h}
ν_1 (A_1)	(R)	A (IR, R)	$3(Ag + Bg)$ (R)
			$3(Au + Bu)$ (IR)
ν_2 (E)	(R)	$2A$ (IR, R)	$6(Ag + Bg)$ (R)
			$6(Au + Bu)$ (IR)
ν_3, ν_4 (F_2)	(IR)	$3A$ (IR, R)	$9(Ag + Bg)$ (R)
			$9(Au + Bu)$ (IR)

TABLE IV

ASSIGNMENT OF THE IR SPECTRUM OF $NaNiFe_2(AsO_4)_3$

Mode	Frequency (cm⁻¹)
ν_1 (A_1) AsO_4	860
	901
ν_3 (F_2) AsO_4	820 (sh)
	789
	700 (w)?
	592[a]
ν_4 (F_2) AsO_4	496[a]
$+$	474[a]
ν_2 (E) AsO_4	447 (sh)
$+$	
Lattice modes	390
	334

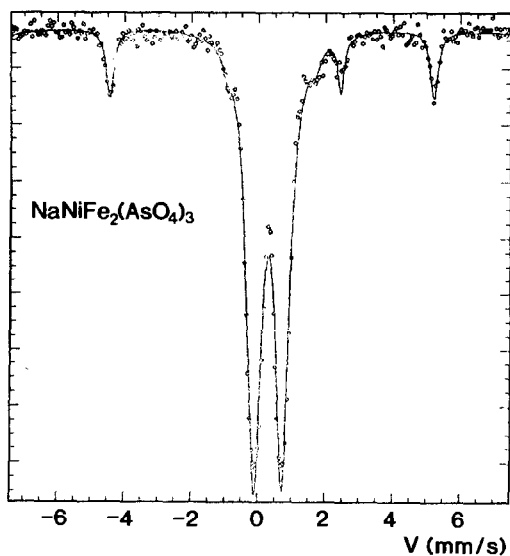*Note.* sh, shoulder; w, wide.
[a] ν_3, ν_4 (F_{1u}) FeO_6.

FIG. 2. Mössbauer spectrum of NaNiFe$_2$(AsO$_4$)$_3$.

The bands at 496 and 474 cm^{-1} too enclose the F_{1u} modes corresponding to the FeO$_6$ polyhedra without the splittings expected for condensed structures with strong interactions among the polyhedra. In spite of structural similarity this vibrational behavior turns out to be different from that of the CrO$_6$ groups in the homologous series, whose compounds produce better-defined bands and in which very strong couplings with the AsO$_4$ tetrahedra are observed.

The fact that Ni–O stretching vibrations are not appreciated in the zone correspondent to the octahedric symmetry, at 500 cm^{-1}, is attributed to the existence of bridges between the polyhedra of this divalent cation without Oh symmetry. This behavior is similar in all these compounds with M^{III} = Fe or Cr and M^{II} = Mg, Ni, Co, Cu, and Zn (8, 11).

3.3. Mössbauer Spectrum

The Mössbauer spectrum (Fig. 2) displays a central quadrupole doublet and 20 ± 2% abundant magnetic sextet. The magnetic signal belongs to unreacted α-Fe$_2$O$_3$ used in the preparation. The central doublet could be fitted only with two quadrupole sites.

In compounds of a series of oxoanions of this type the Fe(II) and Fe(III) were observed (14). The present isomer shifts correspond only to Fe(III) in the lattice, but in two positions of equal population in surroundings with different distortion degrees as revealed by the parameters shown in Table V. Similar values have also been reported for other oxidic systems containing ferric ions in octahedral oxidic coordination (15, 16). The value of the quadrupolar splitting demonstrates a greater distortion of the oxygen polyhedra than that found in other oxidic systems.

The present results that show the presence of two sites for Fe(III) in the lattice are the first direct evidence of the difference between this structures and others of the distorted langbeinite type, where the trivalent cation occupies only the site of C_3 symmetry (17).

4. Conclusions

NaNiFe$_2$(AsO$_4$)$_3$ is the only phase of this type with Fe(III) to crystallize a monoclinic lattice with space group $P2_{1/c}(C_{2h}^6)$. From the spectroscopic study we conclude that the monoclinic lattice of NaNiFe$_2$(AsO$_4$)$_3$ is formed by three kinds of polyhedra: AsO$_4$ tetrahedra in general C_1 sites, distorted FeO$_6$, and Ni–O polyhedra without Oh symmetry.

The analysis of the ^{57}Fe Mössbauer spectrum has shown that the cation M^{III} occu-

TABLE V

^{57}Fe MÖSSBAUER PARAMETERS FOR NaNiFe$_2$(AsO$_4$)$_3$ AT ROOM TEMPERATURE (VALUES IN mm · sec^{-1})

Q_1	δ_1	Q_2	δ_2
1.04(3)	0.39(1)	0.58(3)	0.40(1)

pies two different sites in surroundings with different distortion degrees, opposed to what happens in orthorhombic distortion, in which such a cation occupies only C_3 sites. More evidence of this structural difference is the nonexistence of couplings in the IR spectrum among the vibrational modes of the polyhedra of the lattice, observable in molybdates, vanadates, and arsenates with orthorhombic structure (5, 8, 17). Thus, the monoclinic phase is less condensed than the orthorhombic.

The vibrational behavior of the AsO_4^{3-} ion also is simpler than that of the double and triple vanadates and phosphates of similar structure, which usually present little defined IR spectra, owing to more complex lattice distortions (18, 19). The ^{57}Fe Mössbauer measurements indicate that the electronic delocalization which involves different metal–oxygen polyhedra is less strong than that in phosphates with a highly condensed structure.

Acknowledgments

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