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X-RAY AND NEUTRON SINGLE-CRYSTAL STUDY OF *P4/n* VESUVIANITE

ALESSANDRO PAVESE[1]

Dipartimento di Scienze della Terra, Università di Milano, Via Botticelli 23 I-20133 Milano, Italy

MAURO PRENCIPE[1] AND MARIO TRIBAUDINO[1]

Dipartimento di Scienze Mineralogiche e Petrologiche, Università di Torino, Via Valperga Caluso 35 I-10125 Torino, Italy

STEEN SØRENSEN AAGAARD[1]

Risø National Laboratory, DK-4000 Roskilde, Denmark

ABSTRACT

Single-crystal X-ray- and neutron-diffraction refinements (R = 3.9% and 6.6%, respectively) were performed on a sample of $4/n$ vesuvianite [a 15.532(1), c 11.821(1) Å, V 2851.7(5) Å^3] from a rodingite in Val d'Ala, Piemonte, Italy. The results demonstrate an ordered distribution of Ca over Ca(4)*a,b* and of Fe over *M*(3)*a,b* sites, whereas no preference is shown by Al, Fe and Mg atoms at *M*(2)*a,b* sites. Moreover, the neutron refinement located five hydrogen positions [H(10)*a,b,c* and H(11)*a,b*], statistically occupied. H(11)*a,b* atoms are bonded to O(11)*a* and *b*, whereas H(10)*a,b,c* atoms are located along the 4-fold axis, and form hydroxyl groups with O(10)*a* and *b*. The presence of hydrogen gives rise to several possible local configurations, leading to complex schemes of order.

Keywords: vesuvianite, X-ray diffraction, neutron diffraction, cation distribution, H-bearing sites, order–disorder.

SOMMAIRE

Nous avons effectué des affinements de la structure d'un échantillon de vésuvianite $4/n$ sur cristal unique par diffraction X et de neutrons, jusqu'à un résidu R de 3.9% et de 6.6%, respectivement. L'échantillon provient d'une rodingite de Val d'Ala, Piemonte, Italie, et possède les paramètres réticulaires a 15.532(1), c 11.821(1) Å, V 2851.7(5) Å^3. Nos résultats indiquent une distribution ordonnée de Ca sur les sites Ca(4)*a,b*, et de Fe sur les sites *M*(3)*a,b*. En revanche, les atomes Al, Fe and Mg ne montrent aucune préférence entre les sites *M*(2)*a,b*. De plus, l'affinement par diffraction de neutrons a permis de localiser cinq atomes d'hydrogène [H(10)*a,b,c* et H(11)*a,b*], dont l'occupation est statistiquement répartie. Les atomes H(11)*a,b* sont liés à O(11)*a* et *b*, tandis que les atomes H(10)*a,b,c* sont situés le long de l'axe de symétrie 4, et forment des groupes hydroxyle avec O(10)*a* et *b*. La présence des atomes d'hydrogène permet plusieurs agencements locaux possibles, ce qui mène à des schémas complexes du degré d'ordre.

(Traduit par la Rédaction)

Mots-clés: vésuvianite, diffraction X, diffraction de neutrons, distribution de cations, sites des atomes d'hydrogène, degré d'ordre.

INTRODUCTION

Two subjects about vesuvianite have drawn the interest of researchers: 1) the extremely complex composition and the structural behavior of cations and anions in the structure, and 2) the structural and thermodynamic features of some anomalous varieties, whose space-group symmetry deviates from *P4/nnc*. Recent work on *4/nnc* vesuvianite clarified the role of boron and fluorine, and yielded a crystal-chemical model of site occupancies in *4/nnc* vesuvianite, using results from both X-ray and neutron single-crystal refinements (Yoshiasa & Matsumoto 1986, Groat *et al.* 1992a, b, 1994a, b, 1996). These data, complemented by NMR, EXAFS and IR measurements (Phillips *et al.* 1987, Ohkawa *et al.* 1992, Groat *et al.* 1995), have provided information on the local configuration around the cations and OH sites.

Observed violations of the symmetry *P4/nnc* motivated refinements of the vesuvianite structure with space-group *P4/n* (Giuseppetti & Mazzi 1983, Fitzgerald

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E-mail addresses: pavese@p8000.terra.unimi.it, prencipe@dsmp.unito.it, triba@dsmp.unito.it, sqrensen@risoe.dk
Correspondence to: Mario Tribaudino.

et al. 1986a, b, 1987) and *P*4 (Allen 1985); thermodynamic and theoretical studies have been performed as well (Allen & Burnham 1992, Groat *et al.* 1993). Allen & Burnham (1992) suggested that low-symmetry vesuvianite consists of a domain structure, with ordered low-symmetry domains of a size sufficient to be revealed by X-ray diffraction. In high-symmetry vesuvianite, the ordered domains are too small to be revealed by X-ray diffraction, and the average structure is observed. In principle, the difference between low-symmetry and high-symmetry vesuvianite arises from different schemes of ordering of the cations filling the channel along the 4-fold axis; the possible distributions are compatible with *P*4/*n*, *P*4*nc* and *P*4 symmetry. TEM evidence of a domain texture (Veblen & Wiechmann 1991) led those authors to suggest that the observed domains are pseudomerohedral twins of monoclinic *P*2/*n* symmetry. The deviation from tetragonal symmetry was further addressed by Groat *et al.* (1993). They suggested that deviation from uniaxial optical behavior could be related to spontaneous strain associated with a tetragonal (*P*4/*nnc*) to monoclinic (*P*2/*n*) transition. In this case, the transition would be not simply driven by cation ordering, but also requires their relaxation off the 4-fold axis in the channel: this is expected to be a secondary effect of the ordering of cations. Therefore, a detailed study of the cation partitioning in the structure of a 4/*n* vesuvianite should provide a key to the crystal-chemical behavior of vesuvianite, and its relations to phase transitions. This is the purpose of our investigation.

BACKGROUND INFORMATION

In low-symmetry vesuvianite, a number of independent cation sites are split into *a* and *b* sites, allowing atomic rearrangement as a result of order–disorder phenomena. As the cation partitioning contributes significantly in stabilizing structures and determining thermodynamic functions, a reliable estimate of the cation distribution in vesuvianite is required for thermodynamic and petrological purposes. However, the extremely complex structure and the large chemical variability, in addition to the limited number of refinements of low-symmetry vesuvianite, make the evaluation of site occupancies a rather complex task.

X-ray- and neutron-diffraction experiments provide useful complementary information, which may be the key for solving such a problem. Owing to different interactions of neutrons and X-rays with matter, combined refinements can provide independent constrains on the site occupancies. Moreover, neutron diffraction allows distinction between quasi-isoelectronic atoms such as Mg, Al and Si , which are present in vesuvianite, and is sensitive to hydrogen contributions. In the case of vesuvianite, it is expected also that hydrogen plays a role in the cation ordering (Valley *et al.* 1985).

Single-crystal X-ray- and neutron-diffraction experiments were performed at room temperature on a 4/*n* vesuvianite sample from Val d'Ala, Piemonte, Italy, to investigate the distribution of cations and to clarify the role of the H atoms. The sample was chosen for 1) its gem quality, 2) the good quality of results previously obtained by Giuseppetti & Mazzi (1983) on a specimen from the same locality, in spite of the low symmetry, 3) the significant order of cations observed by those authors at the Ca(4)*a*,*b* and *M*(3)*a*,*b* sites, which suggests that cation ordering may also have involved other sites.

EXPERIMENTAL

Sample characterization

A single crystal of natural vesuvianite from a rodingitic rock (Mineralogical Collection of the Dipartimento di Scienze della Terra of the University of Milan) was used for the present study. The crystal is prismatic, bounded by {100}, {110}, {001} and {011} forms, with a volume of approximately 150 mm^3. A fragment (0.2 × 0.2 × 0.3 mm) of the large crystal utilized for the neutron-diffraction experiment was subsequently used for X-ray diffraction.

Two thin sections of the sample used for neutron diffraction were cut parallel to (001) and (100), to test for anomalous birefringence (Groat *et al.* 1993) , and to permit chemical analyses by means of the electron microprobe.

Chemical analyses were performed on an ARL SEMQ electron microprobe, with wavelength-dispersion spectrometry (WDS); results are reported in Table 1. Fluorine was sought both by WDS and by energy-dispersion (thin-window) spectrometry; no significant fluorine was detected. The presence of boron was ruled out, as the sample studied clearly falls within the B-free vesuvianite group, according to the criteria pointed out by Groat *et al.* (1992a). The chemical composition basically confirms that from Giuseppetti & Mazzi (1983). All iron was taken as Fe^{3+}, since the very modest amount of Fe^{2+} reported by Giuseppetti & Mazzi (1983) does not affect significantly the site occupancies and charge calculations.

TEM observations were carried out on a powdered sample, deposited on a holey carbon film. A Philips

TABLE 1. COMPOSITION OF VESUVIANITE, VAL D'ALA, ITALY

SiO_2 wt.%	37.24	Si *apfu*	17.95 (24)
Al_2O_3	17.67	Al	10.04 (14)
MgO	2.72	Mg	1.96 (5)
Fe_2O_3	3.16	Fe^{3+}	1.14 (5)
CaO	36.60	Ca	18.90 (38)
subtotal	97.39		50.00
H_2O	2.83		
total	100.22		

The proportion of atoms have been calculated on the basis of 50 cations; the H_2O content has been determined according to the B-free model of Groat *et al.* (1992a). Estimated standard deviations reflect the results of 18 analyses.

CM12 electron microscope, operating at 120 kV and equipped with a double-tilt sample holder, was used.

Single-crystal neutron diffraction

The neutron-diffraction experiment was performed at the 10 MW steady state DR3 reactor at Risø National Laboratory, Denmark, using the TAS2 4-circle neutron diffractometer. The thermal neutron flux at the sample position was 1.5 × 10^6 n/(s cm^2). The monochromatic beam of $\lambda = 1.0462$ Å (band- pass $\Delta\lambda/\lambda \approx 10^{-3}$) was achieved by Bragg reflection from (002) plane of a Be single crystal. The intensity profile of each reflection was measured by a θ–2θ scan, and the collection time was determined by continuously monitoring the incident beam, until a counting threshold was achieved. A series of previous checks demonstrated that each peak was fully encompassed, so as to avoid profile-truncations (Destro & Marsh 1987). The detection bank was equipped with a ^{3}He detector, with which the diffracted signal was counted after collimation by a diaphragm 20 mm in diameter. Only $h \geq 0$, $k \geq 0$ and $l \geq 0$ reflections were collected over the angular range $2° \leq 2\theta \leq 80°$, for a total of 4125 reflections. The diffraction profiles were integrated by the profile-fitting method (Pavese & Artioli 1996), which allows those reflections somehow affected by spurious diffraction-maxima (multiple diffraction and parasitic diffraction-maxima due to instrumentation, for instance) to be detected and removed, and permits recovery of very weak and troublesome signals. The intensities were corrected for absorption ($\mu = 0.297$ cm^{-1}) with a laboratory-supplied routine. A home-adapted version of the UPALS code (Lundgren 1982) was used to perform structure refinements. The data were first corrected for merohedral {110} twinning (Britton 1972); the best R factor was obtained with a 1:1 ratio for the two individuals. The structure refinement was carried out on the basis of 1546 independent reflections ($F_o/\sigma \geq 4$), with a fixed weighting scheme ($1/\sigma^2$), using the type-I isotropic extinction model of Becker & Coppens (1975). Owing to the limited number of unique reflections, only the atomic displacement parameters of hydrogen were treated as being anisotropic. In both neutron and X-ray refinements, the initial coordinates were taken from Giuseppetti & Mazzi (1983). A total of 146 variables were refined, yielding $R = 6.6\%$ and $Rw = 8.6\%$.

Single-crystal X-ray diffraction

A room-temperature collection of single-crystal X-ray data was performed as well. This second diffraction experiment was motivated by the need 1) to establish the actual symmetry of the mineral on the basis of a statistically significant set of F_o values, and 2) to provide a cross-check of the results from the neutron-diffraction refinement.

Cell parameters were obtained using 28 reflections, over the interval 20°–30° in 2θ, and refined without symmetry constraints; the resulting unit-cell edges are: a 15.532(1), b 15.532(1), c 11.821(1) Å; no significant deviation from 90° for α, β and γ parameters was observed.

A total of 6305 intensities were measured on a Siemens P4 single-crystal diffractometer equipped with a graphite monochromator, using Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å); the reflections were collected with the θ–2θ scan mode over the angular range $2° \leq 2\theta \leq 60°$, from *hkl* –5–5–4 to 21 21 16, respectively, with scan speed variable from 2 to 30°/min and a 2:1 peak to background ratio; after standard corrections (absorption, Lp and decay to exposure), they were merged, leading to 4176 independent reflections.

The refinement of the X-ray data was performed with the SHELX–93 package (Sheldrick 1993), using 3037 reflections ($F_o \geq 4\sigma$), with standard weighting scheme ($1/\sigma^2$). Merohedral {110} twinning was taken into account at refinement stage, and the results confirmed those reported above for neutron refinement, that is, a ratio of 1:1 of the two twinned individuals; refinements attempted without taking twinning into account did not converge. The isotropic extinction coefficient was refined as well. Refinements also were performed with the UPALS program; we found no deviation from the results obtained by SHELX–93. The refinement was carried out with an anisotropic ADP (Atomic Displacement Parameters) model for each atom, and yielded final $R = 3.9\%$, $Rw = 4.1\%$ and $GooF = 0.93$; 295 variables were refined. Fractional coordinates and displacement parameters for neutron and X-ray refinements are reported in Table 2.

RESULTS AND DISCUSSION

The symmetry of the Val d'Ala vesuvianite

As discussed in the introduction, the actual symmetry of non-4/*nnc* vesuvianite has been a matter of debate. Therefore, the sample used in this work has been characterized by means of optical and TEM observations, and by statistical analysis of the X-ray intensities.

Optical observations show that: 1) the crystal exhibits a moderate color zoning, its green hue suggesting the occurrence of Fe^{3+} (Fitzgerald *et al.* 1992); 2) it has no anomalous birefringence in the (001) plane; 3) it is basically uniaxial, except for local slight biaxial characters ($2V \leq 10°$), with a negative optic sign. No evidence of chemical zoning was found from electron-microprobe analysis on the same sections.

TEM observations were performed in order to check for the possible presence of domain textures. Veblen & Wiechmann (1991) found in a sample of non-4/*nnc* vesuvianite with anomalous birefringence a domain structure of a scale of nanometers, which was interpreted

TABLE 2. POSITIONAL PARAMETERS AND ISOTROPIC DISPLACEMENT FACTORS OF THE VAL D'ALA VESUVIANITE, FROM NEUTRON- AND X-RAY-DIFFRACTION REFINEMENTS

	NEUTRON-DIFFRACTION REFINEMENT					X-RAY-DIFFRACTION REFINEMENT			
	x	y	z	U_{eq}		x	y	z	U_{eq}
Si(1)a	1/4	3/4	0	0.0066(4)	Si(1)a	1/4	3/4	0	0.0056(6)
Si(1)b	3/4	1/4	1/2	0.0087(4)	Si(1)b	3/4	1/4	1/2	0.0042(6)
Si(2)a	0.6801(3)	0.4604(3)	0.1295(4)	0.0055(9)	Si(2)a	0.6814(1)	0.4602(1)	0.1303(1)	0.0058(4)
Si(2)b	0.4590(3)	0.6803(3)	0.3710(4)	0.0039(9)	Si(2)b	0.4584(1)	0.6796(1)	0.3728(2)	0.0047(4)
Si(3)a	0.3492(3)	0.4164(3)	0.1358(4)	0.0076(9)	Si(3)a	0.3488(1)	0.4129(1)	0.1342(2)	0.0065(3)
Si(3)b	0.4163(3)	0.3495(3)	0.3639(4)	0.0081(9)	Si(3)b	0.4196(1)	0.3496(1)	0.3633(2)	0.0056(3)
Ca(1)	3/4	1/4	0.2520(6)	0.012(1)	Ca(1)	3/4	1/4	0.2498(2)	0.0077(2)
Ca(2)a	0.5434(2)	0.3106(2)	0.1205(3)	0.0057(8)	Ca(2)a	0.5453(1)	0.3117(1)	0.1195(1)	0.0069(3)
Ca(2)b	0.3108(2)	0.5437(2)	0.3807(4)	0.0086(8)	Ca(2)b	0.3100(1)	0.5429(1)	0.3789(1)	0.0075(3)
Ca(3)a	0.6018(3)	0.6816(3)	0.1129(4)	0.019(1)	Ca(3)a	0.5992(1)	0.6784(1)	0.1212(1)	0.0111(3)
Ca(3)b	0.6819(3)	0.6013(3)	0.3872(4)	0.0178(9)	Ca(3)b	0.6853(1)	0.6041(1)	0.3959(1)	0.0127(3)
Ca(4)a	1/4	1/4	0.3523(3)	0.0170(2)	Ca(4)a	1/4	1/4	0.3504(3)	0.0080(4)
Ca(4)b	1/4	1/4	0.15040	0.0170(2)	Ca(4)b	1/4	1/4	0.153(2)	0.0080(4)
M(1)a	1/2	1/2	0	0.0127(1)	*M*(1)a	1/2	1/2	0	0.0056(5)
M(1)b	1/2	1/2	1/2	0.0127(1)	*M*(1)b	1/2	1/2	1/2	0.0056(5)
M(2)a	0.3888(1)	0.6210(1)	0.1258(1)	0.0068(1)	*M*(2)a	0.3865(1)	0.6199(1)	0.1258(2)	0.0029(1)
M(2)b	0.6208(1)	0.3872(1)	0.3743(1)	0.0068(1)	*M*(2)b	0.6228(1)	0.3893(1)	0.3730(1)	0.0029(1)
M(3)a	1/4	1/4	0.0329(1)	0.0159(1)	*M*(3)a	1/4	1/4	0.0315(2)	0.0117(3)
M(3)b	1/4	1/4	0.4691(2)	0.0159(1)	*M*(3)b	1/4	1/4	0.463(1)	0.0117(3)
O(1)a	0.2791(2)	0.6727(2)	0.0845(3)	0.0083(7)	O(1)a	0.2785(3)	0.6725(3)	0.0856(3)	0.008(1)
O(1)b	0.6728(2)	0.2800(2)	0.4146(2)	0.0049(6)	O(1)b	0.6733(3)	0.2814(3)	0.4152(3)	0.006(1)
O(2)a	0.6594(2)	0.3824(2)	0.2215(3)	0.0067(7)	O(2)a	0.6619(3)	0.3840(3)	0.2231(3)	0.0053(9)
O(2)b	0.3828(2)	0.6604(2)	0.2776(3)	0.0088(7)	O(2)b	0.3819(3)	0.6576(3)	0.2822(4)	0.009(1)
O(3)a	0.4517(2)	0.7221(2)	0.0763(3)	0.0076(7)	O(3)a	0.4523(3)	0.7222(3)	0.0759(3)	0.008(1)
O(3)b	0.7225(2)	0.4523(2)	0.4243(3)	0.0064(7)	O(3)b	0.7224(3)	0.4514(3)	0.4251(3)	0.007(1)
O(4)a	0.6065(2)	0.4382(2)	0.0311(3)	0.0075(6)	O(4)a	0.6063(3)	0.4391(3)	0.0332(4)	0.008(1)
O(4)b	0.4374(2)	0.6066(2)	0.4710(3)	0.0061(7)	O(4)b	0.4374(3)	0.6054(3)	0.4724(4)	0.0074(9)
O(5)a	0.3294(2)	0.5143(2)	0.1785(3)	0.0095(7)	O(5)a	0.3273(3)	0.5105(3)	0.1775(4)	0.0089(9)
O(5)b	0.5146(2)	0.3297(2)	0.3222(3)	0.0079(7)	O(5)b	0.5179(3)	0.3315(3)	0.3196(4)	0.0075(9)
O(6)a	0.2712(2)	0.3796(2)	0.0597(4)	0.0124(7)	O(6)a	0.2719(3)	0.3753(3)	0.0573(4)	0.010(1)
O(6)b	0.3802(2)	0.2714(2)	0.4405(3)	0.0108(7)	O(6)b	0.3847(3)	0.2715(3)	0.4379(3)	0.011(1)
O(7)a	0.6726(2)	0.5555(2)	0.1780(3)	0.0075(7)	O(7)a	0.6755(3)	0.5562(3)	0.1825(4)	0.010(9)
O(7)b	0.5550(2)	0.6734(2)	0.3202(3)	0.0097(7)	O(7)b	0.5560(3)	0.6702(3)	0.3261(4)	0.0073(9)
O(8)a	0.4386(2)	0.4092(2)	0.0657(3)	0.0065(7)	O(8)a	0.4398(3)	0.4079(3)	0.0650(4)	0.008(1)
O(8)b	0.4092(2)	0.4394(2)	0.4328(3)	0.0079(7)	O(8)b	0.4092(3)	0.4391(3)	0.4314(4)	0.009(1)
O(9)	0.3550(2)	0.3553(2)	0.2485(3)	0.0069(6)	O(9)	0.3582(4)	0.3515(4)	0.2494(3)	0.0075(6)
O(10)a	3/4	3/4	0.1330(1)	0.011(2)	O(10)a	3/4	3/4	0.1275(6)	0.008(1)
O(10)b	3/4	3/4	0.3645(1)	0.011(2)	O(10)b	3/4	3/4	0.3569(7)	0.012(2)
O(11)a	0.4961(2)	0.5603(2)	0.1375(3)	0.0077(7)	O(11)a	0.4953(3)	0.5600(3)	0.1367(4)	0.0085(9)
O(11)b	0.5606(2)	0.4972(2)	0.3628(3)	0.0091(7)	O(11)b	0.5629(3)	0.4962(3)	0.3649(4)	0.0094(9)
H(10)a	3/4	3/4	0.2133(1)	0.21(4)					
H(10)b	3/4	3/4	0.4448(1)	0.21(4)					
H(10)c	3/4	3/4	0.2841(1)	0.21(4)					
H(11)a	0.4961(2)	0.5603(2)	0.2179(3)	0.26(1)					
H(11)b	0.5606(2)	0.4972(2)	0.2825(3)	0.26(1)					

Anisotropic atomic displacement parameters from X-ray (all atoms) and neutron (only hydrogen atoms) refinements are available from the Depository of Unpublished data, Canada Institute for Science and Technology, National Research Council, Ottawa, Ontario K1A 0S2. The origin is chosen at $\bar{4}$.

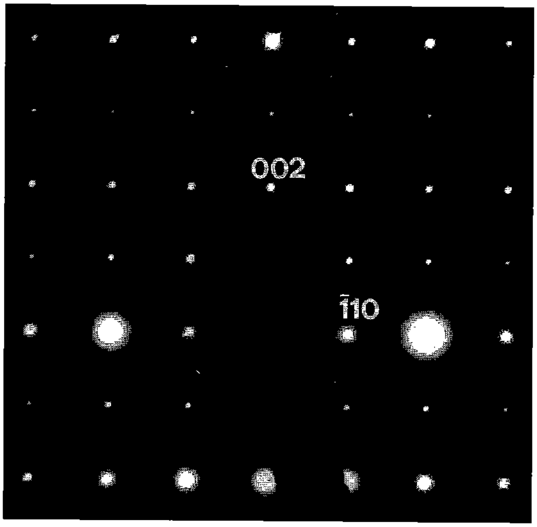

FIG. 1. Selected-area diffraction pattern along [110] in Val d'Ala vesuvianite.

as a twin structure of domains of *P*2/*n* structure. They recognized the presence of non-tetragonal domains by diffuse $l = 2n + 1$ spots in the diffraction patterns and an offset of lattice planes in the HRTEM image. Our TEM observations did not reveal such evidence; the selected-area diffraction pattern obtained along the [110] axis, as reported by Veblen & Wiechmann (1991), does not show any similar diffuse spots (Fig. 1). Moreover, no domain textures were found by HRTEM or by dark-field observation nor, at the scale of the thin flakes examined (*i.e.*, a few micrometers), was any change found in pattern orientation. Obviously, this does not exclude the possibility of larger-scale domains, like the merohedral twinning first found in the Val d'Ala vesuvianite by Giuseppetti & Mazzi (1983) and confirmed by our findings.

Unconstrained unit-cell parameters determined from X-ray single-crystal diffraction do not show significant deviation from tetragonal symmetry; the analysis of the systematic extinctions (Table 3) from X-ray data collection (program EQUIV: Prencipe 1998) identifies *P*4/*n* as the space group most likely for our sample.

TABLE 3. STATISTICAL ANALYSIS OF THE X-RAY INTENSITIES OF FORBIDDEN REFLECTIONS IN SPACE GROUP *P*4/*nnc*

Condition		*N*	$<F^2/\sigma>$
*hk*0:	$h + k = 2n$	128	0.6
0*kl*:	$k + l = 2n$	134	2.5
hhl:	$l = 2n$	18	6.4

N: number of unique reflections; $<F_o^2/\sigma>$: ratio of average intensity to σ.

TABLE 4. SITE OCCUPANCIES, VAL D'ALA VESUVIANITE, AS DETERMINED BY NEUTRON AND X-RAY REFINEMENTS

	Occupancies			
Site	Mg	Al	Fe^{3+}	Ca
M(1)aN	—	1.00	—	—
M(1)bN	—	1.00	—	—
M(2)aN	0.23	0.75	0.02	—
M(2)bN	0.25	0.73	0.02	—
M(3)aN	—	—	0.70	—
M(3)bN	—	—	0.30	—
M(3)aX	—	—	0.85	—
M(3)bX	—	—	0.15	—
Ca(4)aN	—	—	—	0.72
Ca(4)bN	—	—	—	0.28
Ca(4)aX	—	—	—	0.85
Ca(4)bX	—	—	—	0.15

Site occupancies

Cation occupancies at the sites *M*(1)*a,b*, *M*(2)*a,b*, *M*(3)*a,b* and Ca(4)*a,b* (terminology from Giuseppetti & Mazzi 1983) were refined from neutron data (Table 4); the *M*(3)*a,b* and Ca(4)*a,b* site occupancies were independently refined from the X-ray data as well.

The site occupancies were refined from X-ray data after convergence over positional parameters; the cation distribution reported by Giuseppetti & Mazzi (1983) was used as starting point. No significant deviation from the distribution obtained by these authors was observed; in particular: 1) the sums of the unconstrained occupancies of the two Ca(4) and of the two *M*(3) sites are equal to 1.0, respectively, within experimental uncertainties; 2) *M*(3)*a* and Ca(4)*a*, and *M*(3)*b* and Ca(4)*b* site occupancies are statistically equal, and very close to the values obtained by Giuseppetti & Mazzi (1983): 0.83 for *a* and 0.17 for *b* sites. These results confirm, as suggested in previous papers (Allen & Burnham 1992), that *M*(3) and Ca(4) sites are complementary, and that *a* sites are favored in 4/*n* vesuvianite.

Cation partitioning was inferred from neutron data by a non-conventional approach. Each site was treated as a center of independent scattering, and its scattering length was refined, under the constraint to preserve the "total scattering length" of the unit cell, as calculated on the basis of the chemical composition. The actual distribution was subsequently obtained by minimization methods; we relied on simplex and Newton–Rapson techniques (James & Roos 1975), which seek the distribution that best interprets the refined site-scattering lengths, under constraints of chemical composition and site normalization.

The neutron refinement shows a more disordered distribution over *M*(3) and Ca(4) sites than that determined from X-ray data, although the Ca(4)*a* site maintains an occupancy larger than Ca(4)*b*. The average

M(3)–O and Ca(4)–O bond lengths (Table 5) support this observation, since the differences between the interatomic cation–oxygen distances of *a* and *b* sites, from neutron refinements, are smaller than those observed from X-ray data. The discrepancy between X-ray and neutron results vanishes when the cation–oxygen average bond-length of *a* and *b* sites is considered. *M*(1) and *M*(2) site occupancies were refined using neutron-diffraction data only, as Al and Mg are quasi-isoelectronic chemical species. *M*(1)*a* and *b* are completely occupied by Al, in agreement with the *M*–O distances, which are typical of six-coordinated aluminum (≈1.9 Å: Shannon 1976), on the basis of both X-ray and neutron refinements.

According to the neutron data, Al–Mg–Fe cations exhibit a quasi-disordered distribution on the *M*(2)*a* and *b* sites, and the average *M*(2)*a*–O and *M*(2)*b*–O bond lengths are almost equal, consistent with the distribution determined. In contrast, the mean *M*(2)–O bond lengths from X-ray data are significantly different, consistent with a tendency for Mg to enter the *a* site, in accordance with the results of Giuseppetti & Mazzi (1983). As a proof of consistency of the present data, the grand averages of the *M*(2)–O distances from X-ray and neutron refinements are nearly equal, in agreement with the fact that the total occupancy of such sites is the same in both crystals; charge-distribution calculations (Table 6), performed according to Hoppe *et al.* (1989), confirm the distribution determined from the neutron refinement.

TABLE 5. CATION–OXYGEN BOND LENGTHS IN *P*4/*n* VESUVIANITE FROM THE NEUTRON AND X-RAY REFINEMENTS

		a		b	
		X	N	X	N
Si(1)a–O(1)a	×4	1.634(4)	1.626(3)	1.631(4)	1.635(3)
Si(2)a–O(2)a		1.642(5)	1.660(5)	1.634(5)	1.648(5)
–O(3)a		1.635(5)	1.649(5)	1.646(5)	1.639(5)
–O(4)a		1.669(5)	1.668(5)	1.681(5)	1.680(5)
–O(7)a		1.617(5)	1.588(5)	1.620(5)	1.610(5)
mean		1.641	1.641	1.645	1.644
Si(3)a–O(5)a		1.634(5)	1.631(5)	1.637(5)	1.634(5)
–O(6)a		1.609(4)	1.613(6)	1.594(5)	1.614(6)
–O(8)a		1.636(5)	1.622(6)	1.615(5)	1.621(6)
–O(9)		1.670(5)	1.638(6)	1.649(5)	1.666(6)
mean		1.637	1.626	1.624	1.634
Ca(1)–O(1)a	×2	2.327(4)	2.359(3)		
–O(1)b	×2	2.340(4)	2.313(3)		
–O(2)a	×2	2.511(5)	2.518(3)		
–O(2)b	×2	2.531(5)	2.506(3)		
mean		2.427	2.424		
Ca(2)a–O(1)a		2.455(5)	2.482(5)	2.511(4)	2.484(5)
–O(2)a		2.458(5)	2.432(5)	2.394(5)	2.453(5)
–O(3)a		2.368(4)	2.382(5)	2.373(4)	2.363(6)
–O(4)a		2.419(5)	2.451(5)	2.465(5)	2.441(5)
–O(5)a		2.329(5)	2.323(5)	2.339(5)	2.334(5)
–O(5)b		2.423(5)	2.444(5)	2.448(5)	2.450(6)
–O(6)a		3.032(4)	2.933(5)	2.849(5)	2.929(5)
–O(8)a		2.309(5)	2.327(5)	2.314(4)	2.311(5)
mean		2.474	2.472	2.462	2.471
Ca(3)a–O(3)a		2.439(5)	2.453(5)	2.466(5)	2.440(5)
–O(6)a		2.593(4)	2.488(6)	2.384(4)	2.482(6)
–O(6)a		3.027(4)	2.994(6)	2.963(5)	2.998(6)
–O(7)a		2.351(4)	2.375(6)	2.401(4)	2.401(5)
–O(7)a		2.474(5)	2.498(6)	2.516(4)	2.490(5)
–O(7)b		2.516(4)	2.558(6)	2.635(5)	2.578(6)
–O(8)a		2.648(4)	2.615(6)	2.603(5)	2.633(6)
–O(10)		2.595(1)	2.546(4)	2.521(2)	2.554(4)
–O(11)		2.452(4)	2.516(5)	2.560(5)	2.500(5)
mean		2.566	2.560	2.561	2.564
Ca(4)a–O(6)b	×4	2.358(4)	2.300(3)	2.279(9)	2.304(3)
–O(9)	×4	2.595(3)	2.616(3)	2.569(8)	2.584(3)
mean		2.476	2.458	2.424	2.444
M(1)a–O(4)a	×2	1.943(4)	1.948(3)	1.932(4)	1.951(3)
–O(8)a	×2	1.874(4)	1.871(3)	1.881(4)	1.872(3)
–O(11)a	×2	1.867(4)	1.878(3)	1.873(5)	1.875(3)
mean		1.895	1.899	1.895	1.899
M(2)a–O(1)a		1.926(4)	1.945(3)	1.917(4)	1.911(3)
–O(2)b		1.940(4)	1.898(4)	1.875(4)	1.905(3)
–O(3)a		1.979(4)	1.940(3)	1.924(4)	1.966(3)
–O(4)a		2.093(4)	2.070(3)	2.055(4)	2.042(4)
–O(5)a		2.026(4)	1.997(3)	1.966(4)	1.974(3)
–O(11)a		1.934(4)	1.919(3)	1.906(4)	1.952(3)
mean		1.982	1.962	1.940	1.958
M(3)a–O(6)a	×4	2.000(4)	2.064(3)	2.140(5)	2.077(3)
–O(10)a		1.880(8)	1.960(1)	2.132(9)	1.968(2)
mean		1.976	2.043	2.138	2.055

Bond lengths are quoted in Å. The labeling of the oxygen atoms, in the first column, is consistent with *a*-type cations; for *b*-type cations, the *a* label must be changed to *b* (or *vice versa*). Bond multiplicity is shown in the second column.

TABLE 6. ABSOLUTE SITE-CHARGES OF CATION AND OXYGEN IN VESUVIANITE *P*4/*n* FROM VAL D'ALA, DETERMINED ACCORDING TO HOPPE *et al.* (1989) AND FROM THE NEUTRON-DIFFRACTION REFINEMENT

Site	C1	C2	Site	C1	C2	Site	C2	Site	C2
Si(1)a	4.00	3.97	*M*(1)a	3.00	2.91	O(1)a	2.01	O(6)b	1.85
Si(1)b	4.00	3.82	*M*(1)b	3.00	2.91	O(1)b	2.09	O(7)a	1.98
Si(2)a	4.00	4.08	*M*(2)a	2.77	2.74	O(2)a	1.94	O(7)b	1.89
Si(2)b	4.00	4.08	*M*(2)b	2.75	2.81	O(2)b	1.99	O(8)a	2.12
Si(3)a	4.00	4.07	*M*(3)a	2.10	2.25	O(3)a	2.03	O(8)b	2.01
Si(3)b	4.00	4.05	*M*(3)b	0.90	0.94	O(3)b	2.07	O(9)	1.94
Ca(1)	2.00	1.98	H(10)a	0.50	0.52	O(4)a	1.88	O(10)a	1.91
Ca(2)a	2.00	2.00	H(10)b	0.50	0.48	O(4)b	1.91	O(10)b	2.10
Ca(2)b	2.00	1.98	H(10)c	0.50	0.48	O(5)a	1.97	O(11)a	2.17
Ca(3)a	2.00	2.02	H(11)a	0.88	0.80	O(5)b	2.02	O(11)b	2.15
Ca(3)b	2.00	2.01	H(11)b	0.88	0.81	O(6)a	1.85		
Ca(4)a	1.45	1.54							
Ca(4)b	0.55	0.59							

Columns C1 and C2 refer to the charges (in valence units) from the refined partitioning of cations, and from the calculated distribution of charges, respectively.

The observed differences between neutron- and X-ray-derived occupancies and bond lengths in *M*(2), *M*(3) and Ca(4) sites suggest a different distribution of cations in the two single crystals studied: collection of the neutron data was performed on a large crystal, and the results can be considered representative of the average structure over different domains, which have practically the same composition but different patterns of distribution of the cations ("crystallographic zoning"). Such crystallographic heterogeneity may be related to the optical zoning observed in this specimen, without any significant chemical zoning, as confirmed by chemical analyses. This domain structure could somehow be a consequence of the thermal history of the rodingitic rock bearing the vesuvianite sample (Castelli *et al.* 1995 for details). In contrast, X-ray diffraction yields information about the structure of a much smaller and crystallographically homogeneous sample. Further structural investigations are required to clarify the scatter in site occupancies in vesuvianite samples from rodingites.

Hydrogen position

Charge calculations were performed according to Hoppe *et al.* (1989) on the structure from preliminary X-ray refinements, and showed evidence of underbonding of the O(10) and O(11) atoms of oxygen (Table 6). In addition, the combined analyses of neutron and X-ray difference Fourier maps reveal several unresolved residuals in electron density close to the O(10) and O(11) atoms. The initial position of the hydrogen related to O(11) [hereafter H(11)] was suggested by the difference maps and by neutron-diffraction analysis of high-symmetry vesuvianite by Groat *et al.* (1996). Refinement of this position and subsequent splitting into the H(11)*a* and *b* sites were carried out successfully by using neutron data. The atomic displacement parameters for H(11) were constrained to be equal, and H(11)–O(11) distances were fixed to 0.95 Å (see, for instance, Parise *et al.* 1994). Those constraints were required to avoid correlations and unrealistic bond-lengths owing to the large H displacement and the unfavorable coherent to incoherent cross-section ratio of hydrogen, which affects the H contribution to the neutron-diffraction signals.

The H(10) atoms have been located along the 4-fold axis. A plot of the difference Fourier map along this axis shows three H-sites: two bonded with O(10)*b* [H(10)*b,c*] and one, with O(10)*a* [H(10)*a*]. The occupancy of H(10) sites was set equal to 0.5, on the basis of 1) results of the chemical analyses (normalized to 50 cations), 2) tentative H-distributions *versus R*-coefficients, and 3) stoichiometry and electrostatic requirements to be discussed below. The H(10) distribution is consistent with calculations of charge distribution without H contributions, which indicates an undersaturation of O(10) oxygen atoms: O(10)*a* = 1.41 e^-, and O(10)*b* = 1.10 e^-. The refinement of coordinates and anisotropic thermal parameters of H(10)*a,b,c* was performed under constraints similar to those reported for H(11)*a,b*; charge calculations with the proposed structural model, according to Hoppe *et al.* (1989), are reported for oxygen atoms in Table 6. The atomic displacement parameters tensor for H(10) reveals a remarkable anisotropy, with evident elongation along the 4-fold axis. This may be explained as a consequence of partial delocalization along the *c* axis of the hydrogen atom in H(10)*a* and *b*, which is located between O(10)*a* and O(10)*b*. These results, consistent with those from high-symmetry vesuvianite reported by Lager *et al.* (1989), are clearly to be interpreted as representative of average structures; in fact, the presence of a probabilistic distribution of H atoms and of statistical occupancies of *M*(3) and Ca(4) sites leads to a large number of possible local configurations. These may be significantly reduced by the fulfillment of simple electrostatic conditions (Fig. 2): 1) only a single H-atom can be connected to an oxygen atom to form a hydroxyl group, 2) repulsions between H(10)*a* and H(10)*c*, and involving *M*(3), Ca(4) and H sites must be minimized. Two different configurations only ("main configurations"), in which either the *M*(3)*a* and Ca(4)*a* or the *M*(3)*b* and Ca(4)*b* sites are filled, are consistent with minimized *M*(3)–Ca(4) repulsion. For either "main configuration", the H atoms are statistically distributed in order to fulfill the requirements indicated above. In Figure 2, three possible local configurations that satisfy the conditions discussed are shown, and the available H, *M*(3) and Ca(4) sites are given. The positions suitable for hydrogen, along the 4-fold axis, further increase the possible configurations; this fact influences both the configurational contribution to entropy and the energetics of the mineral. In particular, two different H-configurations are compatible with the Ca(4)*a*–*M*(3)*a* sequence (Fig. 2). Hence, order–disorder phenomena involving H-atoms and Mg, Al and Fe cations occur in vesuvianite and have to be taken into account in considering the petrology of vesuvianite-bearing rocks.

CONCLUSIONS

1) The present work demonstrates that 4/*n* vesuvianite from Val d'Ala contains merohedral twinning, with domains exceeding the size of the thin flakes observed by TEM (a few μm).

2) Cation ordering occurs in 4/*n* vesuvianite at Ca(4) and *M*(3) sites, probably as a function of the thermal history of the sample. In contrast, *M*(2) sites show a quasi-disordered distribution of Al–Mg–Fe.

3) Several proton positions are available in 4/*n* vesuvianite, leading to statistical order–disorder schemes.

Order among cations is probably a consequence of the low temperature of formation and the slow rate of cooling experienced by the samples. Vesuvianite formed in contact metamorphic assemblages, which experienced rapid cooling from a high temperature, retain the

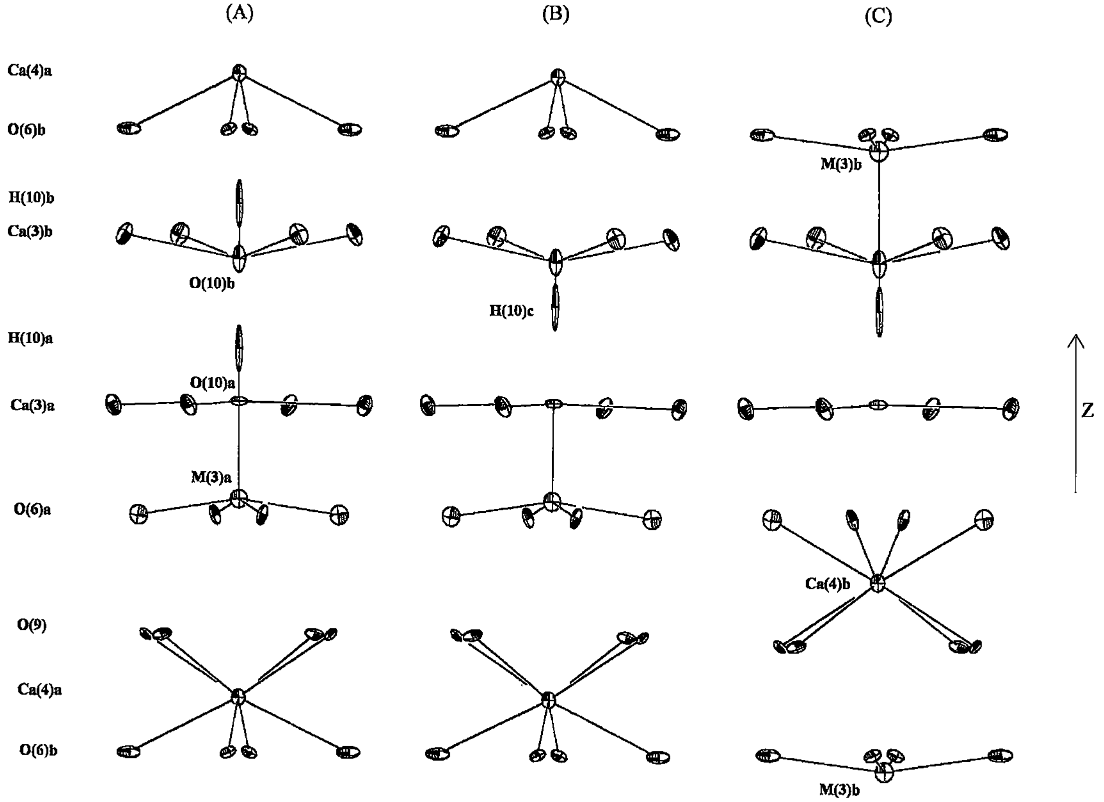

FIG. 2. Structural configurations along the 4-fold axis in the Val d'Ala vesuvianite.

completely disordered 4/*nnc* symmetry (Allen & Burnham 1992). On this basis, the thermal history of the sample can be inferred from degree of cation order, as has been successfully done in the case of orthopyroxenes (Ganguly & Saxena 1987).

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