

Atomic displacement parameters for spessartine $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ and their lattice-dynamical interpretation

Carlo Maria Gramaccioli,^{a*}
Tullio Pilati^b and Francesco
Demartin^c

^aDipartimento di Scienze della Terra, Università degli Studi, Via Botticelli 23, I-20133 Milan, Italy, ^bCNR, Istituto di Scienze e Tecnologie Molecolari, Via Golgi 19, I-20133 Milan, Italy, and ^cDipartimento di Chimica Strutturale e Stereochimica Inorganica, Università degli Studi, Via Venezian 21, I-20133 Milan, Italy

Correspondence e-mail:
carlo.gramaccioli@unimi.it

Received 26 June 2002
Accepted 27 September 2002

A rigid-ion lattice-dynamical treatment accounts reasonably well for most of the atomic displacement parameters (ADPs) reported in the literature for a synthetic sample of spessartine $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$; the model accounts less well for the ADPs of the Mn atom. These results are similar to those obtained for the corresponding garnets pyrope $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ and almandine $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$. The results are confirmed by a very good agreement of the lattice-dynamical estimates with the experimental values of the heat capacity that are currently available, as well as those of the Raman and infrared vibrational spectra. The anomalous behaviour of the Mn atom is reflected in the entropy values. As is the case for pyrope and almandine, here the agreement with the experimental results can be markedly improved if the existence of a low-temperature order–disorder transition concerning the Mn atom is considered. The lattice-dynamical estimates for all the atoms presented here do not agree with the corresponding ADPs obtained in a crystal structure refinement of a supposedly ‘pure’ natural sample from Elba. In turn, these experimental ADPs do not agree with those observed for the synthetic sample, thereby showing a physical difference; such a possibility is in agreement with recent observations by other authors, who found an unexpected fluorine content in several natural specimens of spessartine. Therefore, theoretical estimates of ADPs are reliable enough to point out unexpected situations if disagreement with the observed values occurs.

1. Introduction

Following our interpretation of Raman and infrared spectra, ADPs and thermodynamic functions of several silicate garnets using lattice dynamics (Pilati *et al.*, 1996, here onwards PIL), a corresponding investigation of the Mn–Al garnet spessartine $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ was begun. This investigation was suggested at the time of our first calculations to confirm the similarity of the empirical potentials of Mn and Fe atoms in the 2+ state linked to O, as was suggested by comparison of the isomorphous species tephroite (Mn_2SiO_4) and fayalite (Fe_2SiO_4) in the olivine group (Pilati *et al.*, 1995).

The most important natural garnets can be divided into two groups, each of them characterized by a close structural resemblance and wide miscibility of the end members. For the Ca-rich grossular $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ and andradite $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$, which are the most diffuse members of the so-called ‘ugrandite’ group, PIL observed very good agreement between the experimental values of the ADPs as determined by crystal structure refinement at different temperatures and the corresponding lattice-dynamical estimates; the validity of the

calculations and of the model used were confirmed by the good agreement of Raman and infrared spectra and thermodynamic functions such as the specific heat and entropy.

Matters are more complex concerning the natural Ca-poor garnets belonging to the so-called 'pyralspite' group. For pyrope $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ and almandine $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, the agreement of lattice-dynamical estimates with the experimental data was not entirely satisfactory. In particular, a significant disagreement occurred for the ADPs of the Fe or Mg atoms at the 24c structural site (see Table 5 in PIL). The calculated values were appreciably smaller than the corresponding experimental values.

This 'anomaly' in the ADPs is confirmed by the particular behaviour of the entropy of pyrope and almandine at and above room temperature; the entropy is markedly higher than the corresponding vibrational estimates (even taking account of a magnetic spin contribution for the terms containing transition elements). This discrepancy was interpreted by PIL as being due to 'static disorder'. On the basis of the relatively small ionic radius of Mn^{2+} (like those of Fe^{2+} and Mg^{2+}) with respect to that of Ca^{2+} , a similar problem could be expected for spessartine.

When we began our first calculations (1993), however, no experimental ADPs of this substance were available in the literature for comparison with our theoretical results; a further difficulty was that no sufficiently pure samples were available for study, and we were therefore forced to omit this garnet from our list in PIL.

2. Crystal structure determination

In 1996, a sample of gem-grade spessartine from S. Piero in Campo (Elba Isle) was made available to us due to the courtesy of Dr F. Pezzotta, the curator of the mineralogical collections in the Museum of Natural History in Milan. In spite of the wide contamination in most natural samples, these crystals were reported to be generally very pure, and such a status was apparently confirmed by energy-dispersive X-ray analysis, which revealed the presence of Mn, Si and Al only, without detectable amounts of Fe, Mg or Ca, which are the most common vicariants; for these reasons, the possibility of carrying out an accurate crystal structure determination and refinement was actively considered. Details of the crystal structure determination are given in Table 1.¹

The diffracted intensities were corrected for Lorentz polarization and absorption (North *et al.*, 1968): the transmission factors were in the range 0.70–1.00. After averaging the symmetry-related data, which had an agreement of 2.2% based on F_o , 417 independent reflections were obtained. Of these, 259 with $I > 3\sigma(I)$ and $\theta > 15^\circ$ were considered in the structure refinement (the latter limitation to reduce the effect of secondary extinction, and also to avoid dependence on atomic charge as far as possible in the choice of the scattering

¹Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV0058). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

Crystal data	
Chemical formula	$\text{Al}_2\text{Mn}_3\text{O}_{12}\text{Si}_3$
Chemical formula weight	495.03
Cell setting, space group	Cubic, $Ia\bar{3}d$
a (Å)	11.630 (1)
V (Å ³)	1573.0 (2)
Z	8
D_x (Mg m ⁻³)	4.180
Radiation type	Mo $K\alpha$
No. of reflections for cell parameters	25
θ range (°)	12.20–22.09
μ (mm ⁻¹)	5.31
Temperature (K)	293 (2)
Crystal form, colour	{110}, orange
Crystal size (mm)	0.13 × 0.10 × 0.10
Data collection	
Diffractometer	CAD-4 (Enraf–Nonius)
Data collection method	$\omega/2\theta$ scans
Absorption correction	Empirical
T_{\min}	0.703
T_{\max}	1.000
No. of measured, independent and observed reflections	2701, 417, 289
Criterion for observed reflections	$I > 3\sigma(I)$
θ_{\max} (°)	40.00
Range of h, k, l	0 → h → 20 0 → k → 20 0 → l → 20
No. and frequency of standard reflections	1 every 120 min
Refinement	
Refinement on	F
R, wR, S	0.013, 0.016, 0.84
No. of reflections and parameters used in refinement	259, 40
$(\Delta/\sigma)_{\max}$	0.034
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	0.484, -0.333
Extinction method	Secondary Zachariasen
Extinction coefficient	0

Computer programs used: Enraf–Nonius CAD-4, SDP for Windows.

factors). Scattering factors for neutral atoms and anomalous-dispersion corrections for scattering factors were taken from the *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.3.1. and 2.2b). The refinement of the structure was carried out by full-matrix least-squares analysis using the SDP package of crystallographic programs (Frenz, 1991), minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. The final weights were assigned equal to $1/\sigma^2(F) = 4I/\sigma^2(I)$; the variance of each reflection $\sigma^2(I)$ was assigned according to the function

$$\sigma(F_o) = [\sigma^2(I) + (kI)^2]^{1/2}/(2F_oLp),$$

where $\sigma^2(I)$ is the variance derived from counting statistics and k (= 0.02) is a coefficient for improving the goodness of fit. In the final refinement, a value $g = 8.4 \times 10^{-7}$ was obtained for the coefficient of secondary extinction (Stout & Jensen, 1968). This value is not particularly high, and it has no practical influence on the values of the ADPs. The atomic coordinates are reported in Table 2 and the ADPs in Table 3. In the final difference synthesis, no peaks exceeding 0.48 e \AA^{-3} were found.

Table 2

Refined crystallographic parameters for spessartine from Elba.

Parameters without s.u. values are fixed by symmetry.

Atom	X	Y	Z
Al	0.000	0.000	0.000
Mn	0.000	0.250	0.125
Si	0.375	0.000	0.250
O	0.03473 (5)	0.04789 (5)	0.65210 (5)

3. Calculation procedure

Our calculations proceed according to the ‘classic’ rigid-ion lattice-dynamical model, following the scheme described in PIL and references therein. Using a set of empirical atom–atom functions derived from a best fit to the vibrational frequencies of a group of silicates and oxides, the second derivatives of the potential energy with respect to the (mass-weighted) atomic shifts are calculated. From these derivatives, the so-called dynamical matrices are obtained by summing the corresponding atom–atom terms multiplied by $\exp(-i\mathbf{q}\mathbf{r}_{p-p'})$, where \mathbf{q} is the wave vector and $\mathbf{r}_{p-p'}$ is the distance vector between the atoms p and p' . The process is extended in the reciprocal lattice by varying \mathbf{q} all over the Brillouin zone, which corresponds in practice to the reciprocal primitive unit cell; for the Coulombic contributions, a straightforward process has been adopted (Pilati *et al.*, 1990a).

The square roots of the dynamical matrices correspond to the vibrational frequencies, which unless the model used is invalid should never be imaginary in the Brillouin zone (Gramaccioli & Pilati, 1992) and can be compared with spectroscopic observations (Raman and infrared spectra,

inelastic neutron scattering data). The empirical potentials used correspond to those labelled 4 and reported in Table 3 of PIL, where details about their derivation are given. It is important to remark that in the best-fit procedure to the vibrational frequencies the only substance containing manganese considered was tephroite, Mn_2SiO_4 , an olivine-group mineral.

In all our papers concerning lattice-dynamical subjects, the procedure involving the whole Brillouin zone implies a particular ‘uneven’ sampling, which has been proposed in order to attain considerable reduction of the computing time, since in this way the number of points to be considered in the reciprocal space can be limited to about 100 (Filippini *et al.*, 1976; Pilati *et al.*, 1990b).

As a result of the Brillouin-zone sampling, the phonon density of states $g(v_i)$ is obtained and, using this function [with the ‘normalizing’ condition $\sum_i g(v_i) \Delta v_i = 1$], the estimates of thermodynamic functions become the following, according to well known expressions in statistical mechanics,

$$E = \sum_i E_i = \sum_i g(v_i) \Delta v_i h v_i \{0.5 + [\exp(-h v_i / k T) - 1]^{-1}\},$$

$$S = (E/T) - 3kN \sum_i g(v_i) \Delta v_i \ln[1 - \exp(-h v_i / k T)],$$

$$c_v = \frac{3R \sum_i g(v_i) \Delta v_i (-h v_i / k T)^2 \exp(h v_i / k T)}{[\exp(-h v_i / k T) - 1]^2},$$

where E , S and c_v are the molar estimates of vibrational energy, entropy and the specific heat at constant volume, respectively, k and h are the Boltzmann and Planck constants, N is Avogadro’s number, and T is the absolute temperature.

Table 3

Atomic displacement parameters (as $U_{ij} \times 10^5$) for spessartine.

The form of the temperature factor expression is $\exp\{-2\pi^2 a^{*2} [h^2 U(1, 1) + k^2 U(2, 2) + l^2 U(3, 3)]\}$, where a^* is the reciprocal lattice constant. The isotropic equivalent displacement parameter B_{eq} is defined as $(4/3) a^2 [\beta(1, 1) + \beta(2, 2) + \beta(3, 3)]$. Obs(1) are our data (room temperature) from a natural sample from Elba. The data in columns 3, 5 and 7 have been taken from Geiger & Armbruster (1997), who used a synthetic sample.

	Obs(1)	Obs(293 K)	Cal(293 K)	Obs(100 K)	Cal(100 K)	Obs(500 K)	Cal(500 K)
Al							
$U(1,1)$	443 (8)	320 (10)	319	230 (10)	195	530 (10)	492
$U(1,2)$	−30 (10)	0 (10)	10	20 (10)	0	−0 (10)	2
B_{eq}	0.350 (2)	0.254 (2)	0.252	0.181 (2)	0.154	0.419 (2)	0.388
Mn							
$U(1,1)$	923 (5)	760 (10)	603	345 (7)	264	1340 (10)	1001
$U(3,3)$	476 (8)	330 (10)	410	190 (10)	196	590 (10)	672
$U(1,2)$	174 (8)	260 (10)	32	58 (8)	11	290 (10)	55
B_{eq}	0.611 (2)	0.486 (3)	0.425	0.231 (2)	0.191	0.861 (3)	0.704
Si							
$U(1,1)$	350 (10)	230 (20)	325	170 (20)	186	410 (10)	507
$U(2,2)$	407 (9)	290 (10)	290	200 (10)	169	480 (10)	452
B_{eq}	0.307 (4)	0.214 (4)	0.239	0.150 (3)	0.138	0.361 (4)	0.371
O							
$U(1,1)$	540 (20)	440 (20)	467	310 (20)	294	720 (20)	712
$U(2,2)$	620 (20)	550 (20)	487	380 (20)	306	940 (30)	745
$U(3,3)$	430 (20)	360 (20)	365	230 (20)	240	550 (20)	544
$U(1,2)$	50 (20)	100 (20)	19	50 (20)	13	80 (20)	30
$U(1,3)$	−50 (20)	−100 (20)	−66	−60 (20)	−40	−150 (20)	−108
$U(2,3)$	−40 (20)	10 (20)	7	−20 (20)	10	10 (20)	10
B_{eq}	0.420 (7)	0.354 (7)	0.347	0.243 (7)	0.221	0.583 (8)	0.527

A similar procedure holds for the theoretical evaluation of the ADPs (as \mathbf{U} values); here, in view of the anisotropy, the *eigenvectors* are also important,

$$\mathbf{U}(p) = [Nm(p)]^{-1} \sum_i (2\pi\nu_i)^{-2} E_i \mathbf{e}_i(p) \mathbf{e}_i(p)^{*T},$$

where E_i is the mean energy of the vibrational mode, $\mathbf{e}_i(p)$ is the mass-adjusted polarization vector of the atom p [*i.e.* the portion concerning this atom (three components)] of the i th eigenvector ξ_i of the dynamical matrix corresponding to the mode, and $m(p)$ is the atomic mass; here, owing to vibrational anisotropy, the summation is over the whole Brillouin zone rather than over the density of states (see, for instance, Willis & Pryor, 1975).

4. Vibrational spectra and thermodynamic functions

Before examining the ADPs in detail, it was important to check the performance of the lattice-dynamical model using a number of other physical properties that depend on lattice vibrations, *e.g.* the vibrational spectra and thermodynamic functions.

The values observed by Hofmeister & Chopelas (1991) for the Raman- and infrared-active fundamentals are reported in Table 4, together with the corresponding calculated values: these data clearly show our harmonic lattice-dynamical interpretation of the vibrational spectrum of spessartine to be satisfactory. In particular, the excellent agreement of the A_{1g} frequencies is important, since they are only three in number and there is consequently little possibility of confusion in their assignment. The validity of our empirical potential field reported in PIL is therefore confirmed, the force field of manganese being close to that of iron in the same oxidation state.

Differently from the Raman- and infrared-active vibrational frequencies, the evaluation of estimates of ADPs implies a complete exploration of the Brillouin zone (see above) and provides independent information. As another independent check of the behaviour of our model in the whole

Table 4

Frequencies (cm^{-1}) for infrared or Raman-active modes for spessartine at room temperature.

First line: observed values by Hofmeister & Chopelas (1991) for spessartine. Second line: calculated values for spessartine (this work) using potential No. 4 of Pilati *et al.* (1996). TO: transverse modes; LO: longitudinal modes.

T_{1u} (TO)																	
111	141	167	203	246		316	351	380	412	445	461	520	558	630	861	884	946
	136	152	172	211	271	291	371	397	437	451	501	518	531	595	878	925	942
T_{1u} (LO)																	
115	150	168	212	249		320	352	383	414	531	458	517	593	638	912	871	1030
	136	152	172	223	274	293	372	398	437	468	501	514	576	595	887	942	949
T_{2g}																	
173	194	220	229	300	314	350	472	499	573	628	849	878	1027				
146	190	197	223	324	339	362	461	534	613	645	879	929	1001				
E_g										A_{1g}							
162	318	372	410	521	592	892	913			347	550	905					
148	274	325	403	525	564	839	870			357	549	900					

Table 5

Thermodynamic functions for spessartine ($\text{J mol}^{-1} \text{K}^{-1}$) at different temperatures.

Observed data: specific heat from Geiger & Armbruster (1997) (their synthetic sample) and entropy at 298 K from Holland & Powell (1998). The c_v data have been obtained by subtracting $c_p - c_v = \alpha^2 TV\kappa$ from the observed values. The corrected values for the entropy [S (corr)*] have been obtained by adding the contributions due to both static and magnetic spin disorder to the vibrational estimates.

T (K)	c_v (obs)	c_v (vibr)	S (obs)	S (corr)*	S (vibr)
298	339.5	331.3	367.0	361.3	282.3
320	350.2	345.6	391.6	385.4	306.4
340	360.1	357.3	413.3	406.8	327.8
360	369.8	367.8	434.2	427.5	348.5
380	379.1	377.4	454.5	447.5	368.5
400	387.8	386.1	474.3	467.2	388.2
500	422.9	418.9	565.2	557.2	478.2
600	446.7	439.9	645.0	635.6	556.6

Brillouin zone, thermodynamic properties such as the molar heat c_v and the entropy S were calculated.

The results are reported in Table 5; the observed data for the molar heat are taken from the corresponding c_p data reported by Ottonello *et al.* (1996) and Geiger & Armbruster (1997), corrected by assuming the thermal volume-expansion coefficient α to be 13.86 K^{-1} and the bulk modulus to be 17.90 Pa , as reported by Holland & Powell (1998). The experimental value of entropy at 298 K was also taken from Holland & Powell (1998) and is not a 'third-law' estimate.

In view of the situation concerning the Mn atom, our model assuming a 'static' disorder and reported in PIL for almandine and pyrope was adopted, implying the same contribution to entropy ($\Delta S^\circ = 3R \ln 4 = 34.45 \text{ J mol}^{-1} \text{K}^{-1}$). For the magnetic spin disorder contribution, a value of $\Delta S^\circ = 3R \ln 6 = 44.52 \text{ J mol}^{-1} \text{K}^{-1}$ was assigned on considering the spin of the Mn^{2+} ion.

Taking care of both kinds of disorder, the agreement of the experimental values of both entropy and the specific heat with our theoretical estimates is remarkably good; it is also interesting to observe that our value for the vibrational contribution to entropy at 298 K ($282.3 \text{ J mol}^{-1} \text{K}^{-1}$) is reasonably close to the corresponding value ($283.96 \text{ J mol}^{-1} \text{K}^{-1}$) reported by Ottonello *et al.* (1996) who used a different non-lattice-dynamical approach. Furthermore, it should be considered that no data specific to spessartine besides the atomic coordinates and the unit-cell parameters have been used; even our potentials, which correspond to the 'No. 4' set reported in PIL, were not fitted to any data concerning spessartine.

Therefore, besides confirming the possibility of the existence of site disorder for spessartine

like that for pyrope and almandine, we have reached an indirect proof that spessartine should also undergo an anti-ferromagnetic order–disorder transformation at low temperature.

5. The case of ADPs

Our experimental ADPs are reported in the second column of Table 3, where they are compared with the corresponding lattice-dynamical estimates (fourth column). There is a notable difference between these estimates and our observed data; however, unlike the corresponding situation in pyrope and almandine, this discrepancy concerns more or less all the atoms in the structure and not just the Mn atom. In view of such discrepancies, we initially thought that our calculations were not reliable, most probably because of the inadequately known potentials for the Mn atoms, and for this reason at that time we discarded spessartine from our study, waiting for further developments in the field.

In 1997, during a meeting in Milan dealing with pegmatite minerals, Professor P. Černý announced that many specimens of spessartine from gem-bearing pegmatites, and in particular those from Elba, contain notable and previously unsuspected amounts of fluorine. Moreover, the most fluorine-rich samples are the purest with respect to the possible substitution of Mn and Al with other metals (Černý & Teerstra, 1997).

The presence of fluorine is very probably due to the same mechanism that occurs in hydrogarnets, which are well known substances in which the SiO_4 groups are substituted by four OH groups. However, unlike the hydroxyl groups [where at least in some garnets such a mechanism may proceed up to the complete replacement of SiO_4 by $(\text{OH})_4$] the substitutions $\text{F}_4 \Rightarrow \text{SiO}_4$ are partial, since the F atoms can only act as acceptors of hydrogen bonds; on the other hand, such bonds are necessary to increase the stability of the compound by counterbalancing the absence of the central Si atoms. Owing to all these partial substitutions, the ADPs of several atoms are obviously affected; this usually happens in the sense of an apparent increase of the mean-square displacement, because there is a spread of the average atomic positions, and a partial occupation of the Si site.

Almost at the same time, Geiger & Armbruster (1997) published a work dealing with the crystal structure and thermodynamic properties of spessartine. We were pleased to note that the experimental values of the ADPs reported by these authors for the Al, Si and O atoms in a synthetic sample are reasonably close to our theoretical values at different temperatures, whereas those of the Mn atoms are different and almost show the same situation we had already observed for pyrope and almandine and which we had explained on the basis of static disorder. The situation is particularly evident on comparing the 'isotropic' B_{eq} values.

An important point is that there is a stronger difference between the data set of Geiger & Armbruster (1997) and our own experimental values concerning the natural sample from Elba than there is with respect to our own theoretical estimates, and the difference is significant in terms of the s.u. values; this situation shows that the apparent failure of our calculations was due instead to the existence of a *physical difference* between the garnet from Elba and the synthetic spessartine end member. This difference is most probably connected with the presence of fluorine; unfortunately, such a hypothesis could not be confirmed by a chemical analysis because of the loss of the crystal after collection of the X-ray data. In any case, since there are no doubts concerning the composition of the sample studied by Geiger & Armbruster (1997), the good performance of our model for a pure crystal of spessartine is confirmed (see also above).

Therefore, theoretical estimates of ADPs are reliable enough that whenever disagreement with the observed values occurs there are good motives for considering unexpected possibilities in the examined samples.

References

- Černý, P. & Teerstra, D. K. (1997). *First International Workshop on Petrology, Rare Minerals and Gemstones of Shallow-Depth Pegmatites*, 11–13 September 1997, Museo di Storia Naturale and Società Italiana di Scienze Naturali, Milan, Italy.
- Filippini, G., Gramaccioli, C. M. & Simonetta, M. (1976). *Acta Cryst.* **A32**, 259–264.
- Frenz, B. (1991). *Improved Productivity through Crystallographic Packages, Crystallographic Computing*, pp. 126–135. Oxford University Press.
- Geiger, C. A. & Armbruster, Th. (1997). *Am. Mineral.* **82**, 740–747.
- Gramaccioli, C. M. & Pilati, T. (1992). *Advances in Physical Geochemistry*, edited by S. Saxena, Vol. 10, pp. 241–263. New York: Springer.
- Hofmeister, A. M. & Chopelas, A. (1991). *Phys. Chem. Miner.* **17**, 503–526.
- Holland, T. J. B. & Powell, R. (1998). *J. Metamorph. Geol.* **16**, 309–343.
- North, A. C., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Ottonello, G., Bokreta, M. & Sciuto, P. F. (1996). *Am. Mineral.* **81**, 429–447.
- Pilati, T., Bianchi, R. & Gramaccioli, C. M. (1990a). *Acta Cryst.* **A46**, 309–315.
- Pilati, T., Bianchi, R. & Gramaccioli, C. M. (1990b). *Acta Cryst.* **A46**, 485–489.
- Pilati, T., Demartin, F. & Gramaccioli, C. M. (1995). *Acta Cryst.* **B51**, 721–733.
- Pilati, T., Demartin, F. & Gramaccioli, C. M. (1996). *Acta Cryst.* **B52**, 239–250.
- Stout, G. H. & Jensen, L. H. (1968). *X-ray Structure Determination*. New York: MacMillan.
- Willis, B. T. M. & Pryor, A. W. (1975). *Thermal Motion in Crystallography*, p. 97. Cambridge University Press.