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Thermal Parameters for Minerals of the Olivine Group: their Implication on Vibrational Spectra, Thermodynamic Functions and Transferable Force Fields

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Abstract

Atomic displacement parameters (a.d.p.'s) and vibrational entropies have been calculated for some minerals of the olivine group, such as forsterite (α-Mg_2SiO_4), fayalite (Fe_2SiO_4), tephroite (Mn_2SiO_4) and monticellite ($CaMgSiO_4$), for which accurate experimental data are available; the calculations were also extended to glaucochroite ($CaMnSiO_4$). For these purposes, a rigid-ion Born–von Karman model has been applied, using empirical atomic charges and force fields derived from a best fit to the Raman–IR spectra of all these minerals and to the experimental phonon dispersion curves of forsterite and quartz. The agreement between theoretical and experimental data is remarkably good, even at different temperatures, with the only exception of the displacement parameters of one O atom in monticellite, whose structure has been refined using a set of new data. The present model, whose successful extension to quartz proves a certain degree of transferability to other structural types, implies some reinterpretation of the IR–Raman vibrational spectra, especially for the low frequencies of tephroite and fayalite; agreement with the experimental (crystallographic) a.d.p.'s was essential for checking the validity of the empirical force fields. The values of vibrational entropy for fayalite and tephroite are consistent with complete magnetic disorder above 100 K; for fayalite the corrected Si—O bond lengths (average: 1.633 Å) are essentially temperature-independent under 1173 K.

Introduction

The calculation of a.d.p.'s for crystals can be particularly useful, as it provides the means to verify the physical meaning of the corresponding data obtained from structure refinement; moreover, on these grounds even the general validity of the model can be checked, as well as the force fields employed to interpret the vibrational behaviour of the crystals being studied.

For instance, if accurate experimental values of such thermal parameters are available, then a good agreement with the theoretical results implies a reasonable behaviour of the model in reproducing the frequencies *in the whole Brillouin zone*, for which very few experimental data (such as phonon dispersion curves) are usually available away from the origin.

Although there is considerable difficulty in obtaining accurate values for a.d.p.'s, these parameters at each temperature provide remarkably more detailed data than a few single values of thermodynamic functions, which can often be reproduced satisfactorily even using a quite rough model, such as Debye's or Einstein's. This happens substantially because in general *all the atoms are not of the same type* (as they are considered in the Debye and Einstein models), and also their displacement is anisotropic. All these particulars can be quite helpful in verifying consistency with respect to all possible vibrational modes.

Another point of considerable interest (and of advantage over simpler vibrational models) is the possibility of transferring these force fields to other similar (or even not so similar) substances, *without introducing additional data* (such as the so-called 'characteristic temperature') fitted to the properties of each particular crystalline phase. In case of success, the vibrational spectra and their interpretation, and even thermodynamic functions, may be deduced *a priori* starting from crystal structure data only, which is an important possibility for minerals and similar inorganic solids.

Of the olivine group, forsterite (α-Mg_2SiO_4) has been subjected to the most extensive physical–chemical investigation. For this substance there are examples of accurate X-ray structure determination in the literature, including reliable measurement of the a.d.p.'s (in this respect, see especially Fujino, Sasaki, Takuchi & Sadanaga, 1981; Bocchio, Brajkovic & Pilati, 1986; Langen, 1987). There are also crystal structure data at various temperatures (Smyth & Hazen, 1973; Hazen, 1976): however, at least some of these high-temperature data are not a reliable source of experimental thermal parameters (Pilati, Bianchi & Gramaccioli, 1990). Besides all this, in the literature there are several papers concerning accurate measurement and a selection of fundamentals in IR and Raman spectra (Servoin & Piriou, 1973; Iishi, 1978; Hofmeister, 1987; Lam, Rici, Lee & Sharma, 1990; Chopelas, 1991; Wang, Sharma & Cooney, 1993), as well as phonon dispersion curves (Ghose, Hastings, Corliss, Rao, Chaplot & Choudhury, 1987) and thermodynamic functions (Robie, Finch & Hemingway, 1982; Robie, Hemingway & Takei, 1982).

In addition to experimental measurements, there are also several works concerning the interpretation of the vibrational spectra of forsterite. Of these works, lattice dynamical calculations are the most reliable, since they provide a *quantitative* answer: in this field, fundamental

contributions are due mainly to Iishi (1978), Price, Parker & Leslie (1987*a,b*), Rao, Chaplot, Choudhury, Ghose, Hastings, Corliss & Price (1988), and Patel, Price & Mendelssohn (1991). The first of these authors essentially performed a complete lattice-dynamical calculation limited at the Γ point ($q = 0$), using modified Urey–Bradley force fields (Shimanouchi, 1963) and either a short-range, or a rigid-ion or a polarizable-ion model, respectively. In their lattice-dynamical calculations extended to the whole Brillouin zone, Price *et al.* (1987*a,b*) used instead a shell model, whereas Rao *et al.* (1988) used a 'rigid-molecular' ion model. A lattice-dynamical study on the density of states in fayalite has been published by Price, Ghose, Choudhury, Chaplot & Rao (1991).

For the internal force field in the SiO_4 tetrahedron, both Price *et al.* (1987*a,b*) and Rao *et al.* (1988) essentially used Morse-type potentials for two-body interactions; the first group of these authors also considered three-body interactions as 'bending' force constants. For the force field external to the SiO_4 tetrahedra, and in particular considering the repulsions between nearest-neighbour ions, Buckingham-type potentials were used in most cases. A similar approach has been adopted in modelling the crystal structure of silicates, including not only forsterite, but also other modifications of Mg_2SiO_4, diopside $CaMgSi_2O_6$, *etc.* (see, for instance, Matsui & Busing, 1984; Matsui & Matsumoto, 1985).

With respect to other natural members of the olivine group, which are isostructural with forsterite, for fayalite Fe_2SiO_4 there are interpreted single-crystal IR data (Hofmeister, 1987), as well as Raman data (Chopelas, 1991); for tephroite Mn_2SiO_4 measurements of IR and Raman vibrational spectra are reported by Stidham, Bates & Finch (1976), which are also discussed by Chopelas (1991). For both these structures, there are accurate values of crystal structure parameters, including the a.d.p.'s, which – as for forsterite – were carefully measured in view of electron-density determination (Fujino *et al.*, 1981). For fayalite, crystal structure data at various temperatures are also available (Smyth, 1975), as well as accurate measurement of thermal expansion (Suzuki, Seya, Takei & Sumino, 1981).

A definite subset in the olivine group includes members which can be derived from the minerals mentioned above, only by replacing one out of the two crystallographically independent metal atoms with calcium and keeping the other (at the origin) untouched: in this way, which does not imply disorder, or change of structure type, three new different minerals can be obtained, *i.e.* monticellite $CaMgSiO_4$, kirschsteinite $CaFeSiO_4$ and glaucochroite $CaMnSiO_4$,

Here, the only available symmetry-labelled spectral data consist of single-crystal Raman measurements on monticellite (Chopelas, 1991). Reliable crystallographic works on these minerals include a neutron diffraction

study on $CaMnSiO_4$ by Caron, Santoro & Newnham (1965), whose principal aim consisted of determining the antiferromagnetic properties; then a crystal structure refinement of $CaMgSiO_4$ and $CaMnSiO_4$ by Lager & Meagher (1978) at various temperatures can be mentioned, as well as a crystal structure refinement of monticellite at various pressures (Sharp, Hazen & Finger, 1987).

However, in spite of the high standard of some of these works on monticellite and glaucochroite, no particular interest or care seems to have been taken in determining their a.d.p.'s accurately. For instance, no values of these parameters are mentioned by Caron *et al.* (1965), and only isotropic *B* values are reported by Sharp *et al.* (1987). Anisotropic a.d.p.'s for both these minerals have been determined by Lager & Meagher (1978), but their uncertainty is too large (the e.s.d.'s being often of the same order of magnitude as the corresponding values). Here, since some thermal parameters had to be fixed during the final cycles of refinement (apparently at arbitrary values) in order to prevent the β's from becoming non-positive definite, it would seem that even their accuracy is quite low. Therefore, in order to determine accurate experimental values of the a.d.p.'s we considered the possibility of refining both these structures, using new data.

Experimental measurements

A crystal of monticellite from Crestmore, California, measuring *ca* $0.08 \times 0.08 \times 0.07$ mm, was mounted on a Nonius CAD-4 diffractometer, using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The unit-cell parameters at room temperature are reported in Table 1; derived from a least-squares fit of 25 independent reflections with θ ranging from 7.0 to 12.0°.

For crystal structure refinement, reflections up to a value of θ of at least 40.0° were collected. A total of 3620 diffracted intensities were collected at room temperature (295 ± 1 K) with variable scan speed (maximum scan time for each reflection: 90 s) by exploring the reciprocal space with $0 < h < 20$, $-11 < k < 11$ and $0 < l < 8$. The diffracted intensities were then corrected for Lorentz–polarization and background effects.

An empirical absorption correction was applied by performing a ψ-scan correction (North, Phillips & Mathews, 1968); the transmission factors were in the range 0.97–1.00. After averaging the symmetry-related data, which had an agreement of 2.3% based on F_o, 1270 independent reflections were obtained. Of these, 705 with $I > 3\sigma(I)$ and $\theta > 15°$ were considered in the structure refinement. Scattering factors for neutral atoms and anomalous dispersion corrections for scattering factors were taken from Cromer & Waber (1974) and Cromer (1974), respectively.

The refinement of the structure was carried out by full-matrix least-squares, using the *SDP* package of crystal-

Table 1. *Unit-cell parameters and fractional atomic coordinates for monticellite at room temperature (298 K), with e.s.d.'s in parentheses*

	x	y	z	Multiplicity
Mg	0	0	0	0.5676 (8)
Ca	0.27684 (2)	0.25	-0.02255 (5)	0.5000 (5)
Si	0.08156 (3)	0.25	0.41098 (7)	
O(1)	0.07767 (8)	0.25	-0.2543 (2)	
O(2)	0.44901 (8)	0.25	0.2460 (2)	
O(3)	0.14753 (5)	0.0457 (1)	0.2733 (1)	

$a = 11.1098 (11)$, $b = 6.3894 (9)$, $c = 4.8281 (5)$ Å, $Z = 4$; space group *Pnma*.

Table 2. *Bond distances (Å) for monticellite*

The values are uncorrected for thermal motion; e.s.d.'s are given in parentheses.

Ca—O(1)	2.480 (1)	Mg—O(2^{ii})	2.092 (1)
Ca—O(2)	2.311 (1)	Mg—O(3)	2.124 (1)
Ca—O(3)	2.410 (1)	Si—O(1^{iii})	1.616 (1)
Ca—O(3^i)	2.291 (1)	Si—O(2^{ii})	1.656 (1)
Mg—O(1)	2.192 (1)	Si—O(3)	1.638 (1)

Symmetry codes: (i) $\frac{1}{2} - x, -y, z - \frac{1}{2}$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$; (iii) $x, y, 1 + z$.

lographic programs (B. A. Frenz & Associates Inc., 1980), and minimizing the function $\Sigma w(|F_o| - k|F_c|)^2$. The parameters of the starting model were taken from Lager & Meagher (1978). The final weights were assigned equal to $1/\sigma^2(F_o) = 4I/\sigma^2(I)$; 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 $k (= 0.03)$ is a coefficient for improving the goodness of fit. The extinction correction was applied according to the formula $|F_o| = |F_c|/(1 + gI_c)$, with $g = 2.17 \times 10^{-6}$. The final value of the *R* index $= \Sigma(|F_o| - k|F_c|)/\Sigma|F_o|$ and of the corresponding weighted index $wR = \Sigma w(|F_o| - k|F_c|)/\Sigma w|F_o|$ are 0.014 and 0.016, respectively. The atomic coordinates are reported in Table 1, together with their e.s.d.'s and the multiplicity; the bond distances are reported in Table 2.

In the final difference synthesis, no peak exceeding 0.4 e Å^{-3} was found. Final values of structure-factor calculations are given in Table S1;* the anisotropic a.d.p.'s are given in Table 6, together with their calculated estimates.

The values of the multiplicity have been refined for Ca and Mg: the results (see Table 1) essentially confirm the presence of Ca only in its site, and imply the presence of a certain amount of Fe (12% atomic) in the Mg site. This is close to the analytical results on monticellite from Crestmore, which are available in the literature (Moehl-

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* A list of observed and calculated structure factors have been deposited with the IUCr (Reference: CR0482). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

man & Gonyer, 1934; Lager & Meagher, 1978); all our interatomic distances are in complete agreement with those reported by the latter authors (within the e.s.d.'s), confirming the essential identity in chemical composition. Since the substitution of Mg by up to *ca* 10% atomic Fe does not seem to appreciably influence the value of the experimental a.d.p.'s in forsterite (Bocchio *et al.*, 1986; Pilati *et al.*, 1990), a similar situation is also assumed to occur for monticellite. For this reason, our experimental values for the a.d.p.'s derived from the present refinement are reported in Table 6 for comparison, together with the corresponding values derived from lattice-dynamical calculations.

For glaucochroite, unfortunately, the only specimens available to us [in the collection of CMG and from the USNM (Smithsonian Institution)] did not afford suitable crystals for our purposes.

Procedure of calculation and discussion

In our first lattice-dynamical work on the subject (Pilati *et al.*, 1990), whose principal scope was the calculation of the a.d.p.'s of forsterite, we essentially started from Iishi's RI3 rigid-ion Urey–Bradley field [converted into valence force-field (VFF) parameters], with a readjustment of the Mg—O stretching constant to obtain a better fit to the experimental phonon dispersion curves and to the entropy value at room temperature. A similar VFF model applied to beryllium and aluminium oxides provided a reasonable interpretation of the vibrational spectra, thermodynamic functions and a.d.p.'s of BeO (bromellite), α-Al_2O_3 (corundum) and $BeAl_2O_4$ [chrysoberyl (Pilati, Demartin & Gramaccioli, 1993; Pilati, Demartin, Cariati, Bruni & Gramaccioli, 1993)]: in these papers, full details of our procedure are reported.

The essential success of our calculations enabled us to examine the possibility of extending the application of the VFF we had derived for forsterite to other silicates, or at least within the olivine group. Initially, our calculations were extended to fayalite (Fe_2SiO_4), tephroite (Mn_2SiO_4) and monticellite ($CaMgSiO_4$), using a slight modification of our empirical force field originally derived for forsterite [see function no. (2) in Table 3], which was implemented by readjusting the parameters relative to Mg, Si and O and determining the new parameters relative to Ca, Mn and Fe(+2) atoms: these modifications were derived by fitting the frequencies of the available Raman and IR spectra of all these substances (see Table 4 for a list of references). Whereas the agreement with the spectral data and with the experimental value of entropy are reasonable (see Tables 4 and 9), the results were not considered to be entirely satisfactory, especially with respect to the a.d.p.'s (see Table 6).

Similarly, our first attempts to extend the application of our VFF force field to quartz were not completely successful, even allowing for some readjustment, or also

Table 3. *Empirical potentials*

Force field no.		(1)	(2)
Atomic charge (electrons)			
Si		−1.566	−0.738
Mg		−1.449	−0.875
Ca		−1.256	−1.509
Mn		−1.282	−1.522
Fe^{2+}		−1.189	−1.190
Stretching potentials			
Si—O	A	2671.197	22.831*
	B	0.75610	−2.799
	C	1.65054	1.637
Mg—O	A	99.5203	2.516
	B	1.47964	0.000
	C	2.17169	0.000
Ca—O	A	187.389	2.665
	B	0.98372	0.000
	C	2.41138	0.000
Mn—O	A	218.025	2.556
	B	0.88885	0.000
	C	2.29810	0.000
Fe^{2+}—O	A	131.087	2.556
	B	1.16470	0.000
	C	2.19962	0.000
O—O	A	6.143	528 497†
(< 5.50 Å)	B	0.87475	8364
	C	3.68461	

Bending potentials (mdyn Å rad^{-2})		
O—Si—O	0.399	0.987
	0.033	−0.031

Bending–stretching (mdyn rad^{-1})		
O—Si—O/Si—O	−0.190	0.838
	0.012	0.038

Stretching–stretching (mdyn Å^{-1})		
Si—O/Si—O	0.276	0.020

Bending–bending (mdyn Å rad^{-2})		
O—Si—O/O—Si—O	0.000	0.046
Sharing edges		
	0.000	−0.263
Not sharing edges		

Parameters A, B, C for Morse functions (1) as energy (kJ mol^{-1}) = $A\{exp[-2B(r-C)]-2exp[-B(r-C)]\}$, where r is the distance. For function (2) stretching constants (mdyn Å^{-1}) = $A + B(r - C)$.

Function 1: 29 parameter 'all-Morse' force field fitted to the vibrational frequencies of forsterite FOR (including dispersion curves), fayalite FAY, monticellite MON, tephroite TEP, and quartz QUA (including dispersion curves).

Function 2: 21 parameter VFF fitted to the vibrational frequencies of FOR, FAY, TEP and MON (only Raman- and IR-active frequencies).

Constants K for bending and bending–stretching as: $K = A + B$ (angle 109.4°).

* Stretching potential of the type: K(stretch) $= A + B(d - C)$ (mdyn Å^{-1}).

† 'Lennard–Jones' function as energy (kJ mol^{-1}) $= Ar^{-9} + Br^{-6}$, applied only to distances ranging from 2.80 to 3.50 Å.

including a bending constant for the Si—O—Si bond angle, which exists in quartz, but does not exist in forsterite (Pilati, Demartin & Gramaccioli, 1994). In agreement with other authors (see, for example, Price *et al.*, 1987*a,b*), we found instead that Morse-type potentials behaved substantially better in this respect than bond-stretching VFF constants, and these potentials were used in our final calculations concerning quartz.

Table 4. *Vibrational spectra of olivines* (cm^{-1})

The numbers in parentheses in the calculated values column correspond to the numbers of the force fields in Table 3.

(a)

	Forsterite obs	calc (1)	calc (2)	Monticellite obs	calc (1)	calc (2)
A_g	183	174	178	145	143	147
	226–227	217	215	172	175	190
	304–305	286	268	258	245	237
	329	327	317	275	272	258
	339–340	337	355	307	328	326
	422–424	418	429	402	414	405
	545–546	556	542	534	550	546
	608–609	625	601	589	606	595
	824–826	824	818	818	785	846
	856	851	882	851	875	880
	965–966	931	961	949	905	940
B_{1g}	(226)	193	236	216	220	218
	272–286	285	285	251	243	247
	315–318	310	311	266	274	243
	374–376	389	366	332	340	324
	410–412	419	420	399	406	413
	592–595	597	572	578	569	576
	920–922	905	897	899	907	898
B_{2g}	(192)	207	196	164	164	179
	220–224	239	232	215	201	198
	260–274	293	283	266	257	243
	318	337	321	303	279	298
	383	373	379	333	345	332
	434	440	424	407	422	399
	582–583	614	566	560	579	573
	632	682	608	600	631	595
	838–839	843	824	828	790	852
	866	873	885	855	886	881
	975–976	947	962	954	915	941
B_{3g}	142–175	176	156	141	138	136
	242–244	255	267	243	240	235
	323–324	319	313	263	275	286
	365–368	355	365	327	339	326
	439–441	453	453	411	424	415
	586–588	627	569	572	581	574
	881–884	878	895	879	890	894
B_{1u} (TO)	201	185	164		158	154
	(224)		243		206	195
	274–276	279	264		229	221
	293–295	292	303		324	304
	320	348	321		357	309
	377–381	376	367		393	357
	405–403	399	387		423	358
	421–434	430			464	452
	475	484			509	553
	498–505	509	487		583	579
	601–613	595	551		776	849
			580		896	899
	838–841	810	819		969	942
	950–957	926	899			
	980–993	962	960			
B_{1u} (LO)	201	185	165		160	154
	275–276	287	244		212	199
	298	292	264		237	238
	320–323	358	304		343	304
	386–390	389	347		366	345
	430–438	422	387		398	358
	459–469	473	398		463	395
		509	487		495	452
	544	538	551		514	553
	644–645	621	618		599	620
	840–845	812	820		788	851
	961–964	961	899		965	900
	991–1086	1036	976		980	959

	Forsterite obs	calc (1)	calc (2)	Monticellite obs	calc (1)	calc (2)
B_{2u}(TO)	201	217	169		208	192
	(224)		238		241	236
	274–276	283	254		251	249
	293–296	302	317		300	305
	309–319	304			359	321
	365	376	349		386	348
	412–423	406	403		430	440
	463–483	450	467		484	526
	(502–507)	518	522		868	897
	865–885	857	896			
B_{2u} (LO)	201	217	194		211	202
	276–278	283	238		242	247
	299	302	260		279	253
	316–318	328	346		303	321
	371	406	354		386	347
	453–460	425	404		407	360
	482–489	494	485		452	446
	528–585	565	566		523	583
	957–994	985	911		962	915
B_{3u} (TO)	142–144	138	151		122	114
	(201–224)		254		194	210
	276–280	266	278		279	266
	(294–301)	290	314		300	288
	(352–361)	338	331		337	305
	400	391	362		402	341
	415–421	433	386		417	362
	465	439	469		488	448
	505–510	507	528		505	524
	537	529	587		594	580
		625			779	850
	838–842	824	824		875	886
	880–882	846	884		905	942
	987–993	939	962			
B_{3u} (LO)	144	138	152		123	114
	275–283	273	256		195	210
	300–313	320	289		292	284
	360–376	387	314		337	301
	403–412	416	355		378	330
	438–446	433	364		403	359
	484–493	455	388		423	362
	511–516	518	492		484	459
	572–597	579	566		540	578
		626	588		600	580
	842–845	824	824		779	851
	961–979	938	900		904	902
	992–996	970	902		971	942
R (%)*	3.2	3.1†			3.2	2.6

(b)

	Tephroite obs	calc (1)	calc (2)	Fayalite obs	calc (1)	calc (2)
A_g	124	122	131	119	120	138
	167	162	183	171	163	185
		218	215		218	234
	244	240	245	237	238	260
	291	285	283	289	288	325
	389	388	386	(369)	384	406
	515	515	568	505	511	555
	575	575	587	562	574	594
	808	814	830	814	816	820
	840	857	874	840	866	880
	935	927	931	932	933	942

Table 4 (cont.)

	Tephroite			Fayalite		
	obs	calc (1)	calc (2)	obs	calc (1)	calc (2)
B_{1g}	(137)‡			(113)‡		
	167	172	150	(186)	161	181
	(223)	211	232		224	233
	276	260	273	281	258	292
	304	314	307		321	340
	378	394	394	376	389	405
	555	548	596	549	551	582
	(840)‡					
	892	902	883	900	912	890
B_{2g}	155	153	138	154	154	161
	(203)	168	182	(193)	166	178
		232	256		227	259
	248	250	283	260	250	274
	307	312	296	312	318	345
	393	402	400	384	398	416
	546	557	603	524	551	579
	588	613	604	577	614	607
	809	828	839	822	830	828
	840	872	887	851	879	883
	934	936	936	947	943	944
B_{3g}	119	118	117	(102)‡	126	121
	(244)	226	212	(189)	221	233
	274	250	249	290	261	277
	318	315	322	309	320	348
	401	418	392	405	415	414
	575	577	598	553	580	582
	(808)‡					
	840	881	879	860	893	887
B_{1u} (TO)		129	120		128	129
		168	161	170	171	170
	177	181	177	180	179	188
		226	226	205	227	231
		262	244	249	267	256
	297	293	310	278	286	299
	306	316	328	(346)	320	349
		435	445	455	432	463
	490	466	564	500	463	554
	565	539	572	542	536	573
	815	802	824	819	804	816
	912	924	904	940	928	904
	950	935	929	972	944	939
B_{1u} (LO)		129	120		128	129
		169	161	175	172	171
		184	178	185	181	188
		231	244	223	229	235
		289	310	258	285	296
		315	328	336	319	344
		363	378	360	355	352
		435	447	480	432	464
		466	565	535	463	554
	580	564	614	598	563	610
		803	824	830	806	817
	950	934	904	961	942	904
	1000	1006	958	1018	1009	961
B_{2u} (TO)		119	108		122	143
		155	143	180	172	149
	187	180	170	192	186	178
	240	244	194	241	255	227
	(310)	284	280	280	278	312
	350	351	335	366	357	365
	430	417	422	430	414	440
	480	485	523	457	486	516
	875	864	881	850	877	888
B_{2u} (LO)		119	108		124	143
		155	143	185	172	149
		180	170	199	188	180
	240	244	280	252	272	308
	(310)	284	333	341	324	314
	350	351	339	(387)	362	365
	430	417	426	441	430	447
	480	485	588	523	514	568
	875	864	906	961	963	907
B_{3u} (TO)		108	108	106	108	121
		163	184	170	162	183
	175	179	204	180	176	211
		227	221	206	224	231
	242	239	241	246	245	243
	276	280	247	270	278	272
	340	344	337	346	352	362
	454	469	450	458	464	463
	512	489	537	499	480	528
		562	584	544	562	583
	816	812	831	819	815	823
	860	850	882	864	861	885
	945	934	933	938	940	942
B_{3u} (LO)		109	109		108	123
		164	187	172	165	183
		198	217	184	190	214
		230	240	235	236	231
		280	247	257	278	271
		314	333	325	307	319
	370	346	347	360	353	362
		472	456	478	471	473
		526	581	529	517	571
		563	602	595	563	588
		812	831	830	815	823
	930	931	907	918	934	905
	960	941	933	959	950	942
R (%)*	2.5	3.7†		3.0	3.3†	

Observed data: Forsterite: Servoin & Piriou (1973), Oehler & Gunthard (1969), Iishi (1978), Hofmeister (1987) and Chopelas (1991); monticellite: Chopelas (1991); tephroite: Stidham *et al.* (1976); fayalite: Hofmeister (1987) and Chopelas (1991).

* The value of $R (= \sum |F_o - F_c| / \sum F_o)$ is reported below each column. For forsterite, where measurements obtained by different authors are available, the range of the reported values is indicated.

† Contribution of LO modes not included.

‡ Not included in the optimization process.

The use of Morse-type potentials of the same type we used for quartz also implied a definite improvement of our results for the olivine group, and this induced us to abandon our former VFF potentials in favour of Morse-type functions. In order to consider all the available experimental frequencies, our final force field [no. (1) in Table 3] was actually derived by including the experimental phonon dispersion curves of forsterite and quartz (obtained by Ghose *et al.*, 1987; Dorner, Grimm & Rzany, 1980, respectively), together with the IR and

Table 5. *Points of lower branches of phonon dispersion curves* (cm^{-1})*

q(hkl)				Forsterite obs	calc
0.2	0	0	Σ_1	52	47
				127	122
					187
				203	219
			Σ_2	99	103
			Σ_3	33	32
				170	167
			Σ_4	26	32
				183	192
0.4	0	0	Σ_1	97	91
				105	96
				227	208
			Σ_2	80	85
					183
			Σ_3	64	64
				145	133
			Σ_4	58	61
				175	188
0	0.2	0	Δ_1	96	88
					178
				204	197
				244	234
			Δ_2	130	134
				179	180
				222	210
			Δ_3	61	56
				169	163
				223	213
			Δ_4	59	55
					147
				213	211
					260
					273
				291	285

q(hkl)				Forsterite obs	calc
0	0.4	0	Δ_1	161	155
					163
				191	186
				238	235
			Δ_2	152	154
				168	163
				196	196
				239	263
			Δ_3	115	110
				157	157
				237	232
			Δ_4	111	108
					167
				235	218
				269	245
					264
					275
0	0	0.2	Λ_1	140	123
				167	161
			Λ_2		128
					190
			Λ_3	68	73
					179
			Λ_4	75	69
				163	157
0	0	0.4	Λ_1		178
					186
			Λ_2		160
				176	185
			Λ_3	139	137
					184
			Λ_4	135	134
				185	184

* Observed data (for forsterite) by Rao *et al.* (1988), reported graphically and here interpolated.

Raman spectra of the olivine group. On examining Table 4, the observed IR and Raman-active frequencies of all the minerals in this group so far examined can be compared with the results of our calculations; the agreement is satisfactory. The agreement is also satisfactory with respect to the experimental data on phonon dispersion curves (Table 5).

The inclusion of the phonon dispersion curves for quartz and forsterite in our fitting process actually *improved* the overall agreement of our calculations with the Raman and IR spectra, even for the other substances, and helped in finding a reasonable interpretation of the vibrational spectra, especially for tephroite and fayalite: after including these data, some inconsistencies in the reported values and attribution of the frequencies were already evident during the early stages of the minimization procedure.

This happened because, as we have seen, the spectral data for the other members of the olivine group are not so complete and exhaustive as for forsterite, and even the interpretation of fundamental frequencies given by the different authors can be questionable at times, especially if this was carried out without an overall consistent model. For instance, a few of the observed Raman frequencies for tephroite and fayalite, which are considered as fundamental by Stidham *et al.* (1976) or by Chopelas (1991), respectively, could not be obtained in any way from our calculations with a consistent field, and if any interpretation of this kind was forced by trying to fit our potentials, then very unrealistic calculated values of other data, such as other frequencies, or thermal parameters or/and thermodynamic functions were obtained.

Most of these Raman frequencies are generally weak or high, with marked probability of corresponding to overtones or to combination levels in general; however, some correspond to strong peaks, such as the B_{3g} band (in our reference system: B_{2g} in other authors' notation) at 808 cm^{-1}, or the 840 and 809 cm^{-1} B_{1g} (B_{3g}) bands for tephroite. In this case, since the strongest A_g peaks are observed for the same substance at 808 and 839 cm^{-1}, respectively, the presence of these peaks can be ascribed to an incomplete extinction of these A_g modes in the polarization: in Chopelas' (1991) review and comparison of all these Raman spectra, they are also omitted.

There are, however, a few strong low-frequency peaks present in the spectra of these minerals (here 100–250 cm^{-1}), which could not match theoretical interpretation. This disagreement is serious, because low-frequency modes are in fact most important for deriving

either the thermal parameters or thermodynamic functions of these substances (see, for instance, Pilati, Demartin & Gramaccioli, 1993), and unfortunately the measurements just in this region are generally not as accurate as they are in other regions of the spectra. Here, for instance, problems of interpretation are found especially for one B_{1g} (B_{3g}) peak reported for tephroite at 137 cm^{-1}, or for the B_{1g} (B_{3g}) and the B_{3g} (B_{2g}) peaks of 113 and 102 cm^{-1}, respectively, reported for fayalite. In our opinion, these peaks are spurious and could only be ascribed to impurity effects or to incomplete extinction of modes in other polarizations.

In all the controversial cases a direct comparison between the observed spectra of tephroite and fayalite was quite helpful: a striking example of this can be seen in Table 4, as well as in Table 2 of Chopelas' (1991) work. In these tables, the corresponding Raman frequencies of the two minerals usually differ by a few cm^{-1} only, whereas just the questionable cases specified above represent evident exceptions to the rule. Since the values of the atomic mass are close to each other, the similarity of the spectra also indicates a remarkable similarity in the atomic charge and in the force field between Fe^{2+} and Mn^{2+}.

Always referring to Table 3 and Chopelas' (1991) table, the disagreement between the spectral data of Fe_2SiO_4 and Mn_2SiO_4 seems to be especially 'concentrated' in some symmetry types, especially in the B_{xg} groups, whereas for the A_g frequencies the agreement is very good. This effect is clearly linked to the much greater difficulty of measuring the B_{xg} modes with respect to the A_g modes, the latter giving significantly stronger peaks, with particularly high signal-to-noise ratios.

On such grounds, an appropriate weight might be given to some of the symmetry types in the process of force-field optimization. Here no weighting was used, but attention was only fully given to the most significant modes as a pointer towards a reasonable overall solution of the problem; in Table 4 those frequencies marked by an asterisk were excluded from our optimization process, and additional 'suspicious ones' are reported between parentheses. In any case, the need for accurate low-frequency spectral data, as well as phonon dispersion curves, can never be emphasized enough for these substances, and for minerals in general.

Since a considerable number of useful spectroscopic data are still lacking, the possibility of considerably improving our present empirical field on this basis cannot be excluded. This idea is supported by our success in reproducing the values of thermodynamic functions for corundum (α-Al_2O_3), bromellite (BeO) and chrysoberyl (Al_2BeO_4) more accurately than the present article, by using a similar rigid-ion model (Pilati et al., 1993). A possible explanation for this can be given by observing that in these oxides the lowest observed Raman and IR frequencies are around 250 cm^{-1}, and with very few exceptions all of them are considerably above 350 cm^{-1}. This implies that, in general, the lowest frequencies (which are the most important for our purposes) have been measured more accurately than for silicates, where the corresponding values are around 100 cm^{-1}.

The calculated thermal parameters at room temperature are reported in Table 6, together with their experimental counterparts by Fujino et al. (1981) for forsterite, tephroite and fayalite, or with our data for monticellite. With the only exception of monticellite (see below), the agreement is remarkably good when our force field no. (1) is used. Some particulars are interesting: for instance, the high experimental value of U's (especially U_{11}) for the atom Mn(1) in tephroite compared with the other metal atom Mn(2) is very well reproduced in our calculations; in spite of the general similarity of the crystal structure and of the observed vibrational frequencies (see above), the corresponding difference between the a.d.p.'s of Fe(1) and Fe(2) in fayalite is not quite so large, which is also reproduced in the calculations. Another interesting point is that the Si and O atoms in tephroite and fayalite have substantially larger U's than the corresponding atoms in forsterite, which appears in both the experimental and in the calculated values. With respect to our previous calculations for forsterite (Pilati et al., 1990), which used a different force field, the agreement between the calculated and the observed U's remains substantially the same.

Although the experimental thermal parameters at different temperatures are reported for forsterite and fayalite by Smyth & Hazen (1973) and Smyth (1975), respectively, these data are not always reliable. For instance, at room temperature they disagree not only with our calculations, but even with the other experimental data, e.g. Fujino et al.'s (1981), which are the most accurate. This disagreement has already been indicated by us for forsterite (Pilati et al., 1990), and leads to an unfortunate situation since it would be especially useful to compare our results with the corresponding experimental data at different temperatures.

For forsterite the disagreement between experimental and our calculated thermal parameters at various temperatures is substantial; for fayalite, however, the disagreement with respect to Smyth's (1975) experimental values is not excessive: it almost concerns the anisotropic behaviour of the a.d.p.'s, whereas the equivalent B's are essentially reproduced (see Table 7). Although in many instances a systematic disagreement is hardly significant in view of the large standard deviation, there is also some evidence for an error which occurred in establishing the exact crystal shape and/or orientation in the numerical integration procedure for absorption correction, whereas the average size was accounted for correctly.

Since our procedure (Pilati et al., 1990) provides not only thermal motion tensors $U_p = \langle u_p u_p^T \rangle$, relative to the

Table 6. *Thermal parameters* ($\times 10^4$)

The temperature factor is in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots\ldots + 2U_{23}klb^*c^*)]$. The numbers in brackets in the calculated values column correspond to the numbers of the force fields in Table 3 used for the calculations.

		U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}	B_{eq}
Forsterite								
Mg(1)	obs	71 (1)	−11 (1)	−1 (1)	47 (1)	−6 (1)	45 (1)	0.45
	calc (1)	69	−8	0	46	−5	48	0.43
	calc (2)	73	−9	−4	60	−4	57	0.50
Mg(2)	obs	49 (1)	0	2 (1)	60 (1)	0	59 (1)	0.44
	calc (1)	48	0	3	53	0	55	0.41
	calc (2)	55	0	3	62	0	61	0.47
Si	obs	44 (1)	0	0 (1)	42 (1)	0	30 (1)	0.30
	calc (1)	42	0	1	38	0	32	0.29
	calc (2)	44	0	1	44	0	32	0.32
O(1)	obs	62 (2)	0	1 (2)	56 (3)	0	34 (3)	0.40
	calc (1)	67	0	2	55	0	39	0.42
	calc (2)	61	0	0	60	0	31	0.40
O(2)	obs	43 (1)	0	−1 (2)	60 (1)	0	50 (1)	0.40
	calc (1)	48	0	0	56	0	51	0.40
	calc (2)	43	0	−1	60	0	47	0.39
O(3)	obs	63 (1)	15 (1)	2 (1)	51 (1)	−3 (1)	51 (1)	0.44
	calc (1)	63	10	2	53	−3	50	0.44
	calc (2)	58	9	4	47	0	46	0.40
Monticellite								
Ca	obs	59 (1)	0	3 (1)	63 (1)	0	71 (1)	0.51
	calc (1)	56	0	3	60	0	68	0.48
	calc (2)	60	0	4	58	0	55	0.46
Mg	obs	72 (1)	−6 (1)	−8 (1)	61 (1)	−16 (i)	56 (1)	0.50
	calc (1)	70	−4	−6	54	−7	56	0.47
	calc (2)	70	−6	−3	63	−4	62	0.51
Si	obs	62 (1)	0	2 (1)	56 (1)	0	43 (1)	0.43
	calc (1)	50	0	−1	45	0	39	0.35
	calc (2)	49	0	1	47	0	36	0.34
O(1)	obs	99 (3)	0	−3 (3)	101 (3)	0	47 (1)	0.65
	calc (1)	71	0	−2	66	0	46	0.48
	calc (2)	78	0	2	72	0	35	0.43
O(2)	obs	59 (3)	0	−1 (3)	92 (3)	0	69 (3)	0.58
	calc (1)	55	0	0	70	0	58	0.48
	calc (2)	49	0	−3	69	0	52	0.45
O(3)	obs	81 (2)	13 (2)	4 (2)	68 (2)	2 (2)	75 (2)	0.59
	calc (1)	71	8	2	55	1	60	0.49
	calc (2)	65	9	4	51	−3	55	0.45
Tephroite								
Mn(1)	obs	107 (1)	−24 (1)	−3 (1)	67 (1)	−11 (6)	62 (1)	0.62
	calc (1)	101	−14	−3	65	−8	64	0.60
	calc (2)	70	−2	−13	55	−1	82	0.54
Mn(2)	obs	59 (1)	0	2 (1)	70 (1)	0	73 (1)	0.53
	calc (1)	63	0	1	69	0	70	0.53
	calc (2)	60	0	6	74	0	57	0.50
Si	obs	51 (2)	0	3 (1)	54 (1)	0	40 (3)	0.38
	calc (1)	58	0	2	52	0	43	0.40
	calc (2)	45	0	0	44	0	33	0.33
O(1)	obs	88 (4)	0	4 (3)	76 (4)	0	40 (3)	0.54
	calc (1)	87	0	2	74	0	50	0.56
	calc (2)	69	0	−1	68	0	34	0.45
O(2)	obs	55 (3)	0	−1 (3)	85 (4)	0	66 (3)	0.54
	calc (1)	64	0	1	76	0	67	0.55
	calc (2)	52	0	−12	71	0	60	0.48
O(3)	obs	68 (3)	21 (2)	4 (2)	67 (2)	−3 (2)	69 (2)	0.58
	calc (1)	82	11	4	66	−1	64	0.56
	calc (2)	68	10	9	54	−7	56	0.47
Fayalite								
Fe(1)	obs	86 (1)	−10 (1)	2 (1)	60 (1)	−8 (1)	51 (1)	0.52
	calc (1)	87	−13	2	59	−5	56	0.53
	calc (2)	64	−5	−7	55	−3	57	0.46
	obs†	105 (6)	−13 (3)	5 (5)	66 (4)	−9	41 (4)	0.56
Fe(2)	obs	54 (1)	0	0 (1)	58 (1)	0	69 (1)	0.47
	calc (1)	55	0	1	61	0	64	0.48
	calc (2)	50	0	3	64	0	53	0.44
	obs†	72 (6)	0	0 (3)	64 (4)	0	53 (4)	0.50
Si	obs	52 (1)	0	1 (1)	52 (1)	0	38 (1)	0.37
	calc (1)	48	0	2	49	0	38	0.35
	calc (2)	42	0	1	45	0	31	0.31
	obs†	67 (11)	0	5 (8)	64 (9)	0	22 (7)	0.40

Table 6 (cont.)

		U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}	B_{eq}
O(1)	obs	83 (3)	0	2 (3)	71 (3)	0	40 (3)	0.51
	calc (1)	76	0	3	70	0	45	0.50
	calc (2)	61	0	0	63	0	31	0.41
	obst	78 (22)	0	40 (23)	92 (23)	0	31 (18)	0.53
O(2)	obs	52 (3)	0	0 (2)	85 (3)	0	63 (3)	0.53
	calc (1)	55	0	0	73	0	61	0.50
	calc (2)	43	0	−4	63	0	49	0.41
	obst	100 (22)	0	15 (18)	54 (19)	0	7 (18)	0.42
O(3)	obs	88 (2)	26 (2)	4 (2)	66 (2)	−4 (2)	67 (2)	0.58
	calc (1)	76	13	4	64	−1	59	0.52
	calc (2)	58	9	4	50	−2	47	0.41
	obst	61 (17)	23 (8)	−8 (13)	84 (26)	−7 (13)	41 (14)	0.49
Glaucochroite								
Ca	calc (1)	56	0	3	59	0	68	0.48
Mn	calc (1)	85	−8	−7	60	−10	62	0.54
Si	calc (1)	51	0	0	46	0	40	0.36
O(1)	calc (1)	82	0	0	73	0	47	0.53
O(2)	calc (1)	58	0	0	71	0	62	0.50
O(3)	calc (1)	74	9	3	57	0	63	0.51

Observed data from Fujino et al. (1981) for forsterite, tephroite and fayalite, or from Smyth (1975) for fayalite at 293 K (marked † in table); our data for monticellite and glaucochroite. A minimum estimate of 1 in the last digit for the standard deviation has been assumed, although in several cases the reported values are sensibly smaller. The a.d.p.'s are referred to the atoms and the unit-cell parameters correspond to our reference (Pilati et al., 1990).

same atom p, but also the tensors $U_{pp'} = \langle u_p u_{p'}^T \rangle$ between different atoms p and p', then the experimental bond lengths can be corrected for thermal motion in the most general case, using the procedure indicated by Scheringer (1972) or by Johnson (1980) [see also Filippini & Gramaccioli (1989)].

The results are shown in Table 8: here, the average Si—O bond length, after correction for thermal motion, indeed remains essentially constant with respect to temperature, at least within the presumed significance of these data (3σ). As expected, the observed shortening of these bonds on increasing temperature is essentially only apparent due to the effect of thermal libration, which in this case approaches that of a rigid body [for more details, see for instance our discussion of Schomaker–Trueblood's (1968) fit to the SiO_4 tetrahedron in forsterite in Pilati et al., 1990]. Considering the uncertainty of these values to be around 0.002 Å, the corrected average Si—O bond length (1.633 Å) is not significantly different from the corresponding corrected value for forsterite at room temperature (1.635 Å).*

The calculated values of entropy for forsterite, tephroite and fayalite as a function of temperature are reported in Table 9. For tephroite and fayalite, contributions of $2R\ln 6$ (29.68 J mol^{-1} K^{-1}) and $2R\ln 5$ (26.76 J mol^{-1} K^{-1}), respectively, have been added to the vibrational estimate: these contributions correspond to complete spin disorder achieved in line with low-temperature transitions from an antiferromagnetic

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* In this case, unfortunately, more accurate data would be needed, since we are just at the limit of significance; however, the general trend is clearly in this sense (the highest discrepancy at 873 K derives from bond distance values which have been estimated too high, and does not involve thermal parameters).

Table 7. Equivalent B (Å^2) for fayalite at various temperatures [observed data from Smyth (1975)]

	293 K		573 K		873 K		1173 K	
	obs	calc	obs	calc	obs	calc	obs	calc
Fe(1)	0.57 (1)	0.53	1.14 (4)	0.99	1.84 (6)	1.56	2.78 (8)	2.11
Fe(2)	0.50 (1)	0.47	1.03 (4)	0.91	1.63 (6)	1.44	2.35 (8)	1.97
Si	0.41 (1)	0.35	0.74 (8)	0.65	1.09 (9)	1.03	1.6 (1)	1.38
O(1)	0.53 (2)	0.50	0.9 (2)	0.91	1.4 (2)	1.42	2.0 (3)	1.93
O(2)	0.42 (2)	0.50	0.9 (2)	0.90	1.2 (2)	1.39	1.9 (3)	1.91
O(3)	0.49 (2)	0.52	0.9 (1)	0.99	1.5 (2)	1.54	2.3 (2)	2.21

Table 8. Si—O bond distances (Å) at various temperatures for fayalite (experimental data from Smyth, 1975) before and after correction for thermal libration

	293 K	573 K	873 K	1173 K
Si—O(1)	1.636 (5)	1.630 (6)	1.635 (7)	1.646 (11)
corrected	1.639	1.636	1.643	1.657
Si—O(2)	1.652 (4)	1.658 (5)	1.664 (7)	1.660 (10)
corrected	1.655	1.663	1.672	1.670
Si—O(3)	1.612 (3)	1.604 (4)	1.605 (5)	1.587 (7)
corrected	1.616	1.611	1.615	1.603
Average	1.628	1.624	1.627	1.620
corrected	1.631	1.630	1.636	1.633

(ordered) structure to the paramagnetic (disordered) structure stable under ordinary conditions (Robie, Finch & Hemingway, 1982; Robie, Hemingway & Takei, 1982; Ulbrich & Waldbaum, 1976). In general, for forsterite the agreement of our calculated data with the corresponding experimental values is quite good, being of the order 1% or less in the range 300–1200 K, and increasing to ca 4% for lower temperatures (down to 100 K), or even more substantially around 50 K. These values are apparently less satisfactory than those obtained in our former work (Pilati et al., 1990); however, there the field was fitted to the value of

Table 9. *Values of entropy* $(J mol^{-1} K^{-1})$ *at various temperatures**

Temperature (K)	Forsterite calc	Forsterite obs	Tephroite calc	Tephroite obs	Fayalite calc	Fayalite obs
50	1.8†	1.8	35.7	28.8	32.2	19.1
100	13.7†	13.1	58.8	56.1	54.9	50.7
200	54.7	53.2	112.0	110.3	108.0	104.3
250	76.1	74.4	136.2	134.7	132.2	128.9
298	95.3	94.1	157.3	155.9	153.0	151.0
	99.6‡	94.0§	155.0‡		146.0‡	150.9§
400	133.1	132.0	197.1	196.2	193.0	193.0
600	194.4†	192.0	258.1	258.6	255.3¶	258.4
800	241.8†	238.1	304.5	306.8	302.1¶	308.3
900	261.1†	258.0	324.0	327.2	321.8¶	329.7
1000	278.6†	276.2	341.6	345.8	341.5¶	349.2
1200	310.9†	308.7	372.4	378.4	372.1¶	384.4

	obs	calc
Monticellite at 298 K	108.30§	106.7
		108.0‡

Glaucochroite at 298 K	137.7

* The calculated values have been obtained from our force field No. 1, and assuming a constant magnetic contribution of $2R\ln 6$, $R\ln 6$ and $2R\ln 5$ for tephroite, monticellite and fayalite, respectively. Observed values by Robie *et al.* (1982); at room temperature, the reported uncertainty is about $0.2 J mol^{-1} K^{-1}$ for fayalite.

† These values were calculated using the crystal structure data at 77 K (Hazen, 1976), or at about 623, 948 and 1273 K (Smyth & Hazen, 1973; Hazen, 1976), using for each temperature the nearest experimental counterpart; the other values were calculated using the crystal structure data at room temperature.

‡ Calculated using our force field no. (2).

§ Experimental values from Berman (1988).

¶ These values were calculated using the crystal structure data at 573, 873 and 1173 K (Smyth, 1975), using for each temperature the nearest experimental counterpart; the other values were calculated using the crystal structure data at room temperature.

entropy at room temperature, whereas here no fit of this kind was considered. Moreover, here our force field has not been exclusively fitted to the forsterite frequencies, but it has been extended to other substances.

For tephroite and fayalite, the disagreement at 50 K is surely due to the proximity of Néel's temperature, which is *ca* 47 and 65 K, respectively, for the two minerals, and here spin disorder is not yet fully achieved. However, already at 100 K there is substantial agreement (around 7%) between our calculations and the corresponding observed values, in line with the diagrams of magnetic entropy shown by Robie, Finch & Hemingway (1982) and Robie, Hemingway & Takei (1982), which clearly show that complete disorder is reached in practice at about twice the Néel temperature. At higher temperatures (200–600 K), the agreement improves, being around 1–2% for tephroite and 1–4% for fayalite; for temperatures around 1000 K, however, the calculated values of entropy are definitely smaller than their experimental counterparts.

For fayalite this disagreement at the higher temperatures can be explained on the grounds of the possibility of a non-negligible electron contribution for substances containing transition elements: for instance, according to

Burns (1985) and Hofmeister (1987), this contribution should be of the order $1.3 J mol^{-1} K^{-1}$ at room temperature, up to $7.8 J mol^{-1} K^{-1}$ at 1000 K, and the latter value is just about the difference we observed with respect to the experimental data. For tephroite, the use of room-temperature crystal structure data for our calculations up to 1200 K does not include the effect of thermal expansion, and this is also a possible explanation for such a disagreement.

There is another interesting point concerning thermodynamic properties. Apparently, according to some authors (*e.g.* Hofmeister, 1987) and in contrast to Robie, Finch & Hemingway (1982), complete spin disorder for fayalite is not achieved below 680 K. Whereas the improved agreement of our calculations with the experimental data for fayalite on increasing temperature up to 400 K might be explained at least in part on these grounds, in our opinion Hofmeister's (1987) claim needs further proof. This is necessary also because the alleged evidence for the lack of complete disorder below 680 K seems to be based only on the difference between the experimental values of entropy at various temperatures and the corresponding values of vibrational entropy obtained from a statistical mechanical model due to Kieffer (1979, 1980, 1982, 1985), a model which has encountered considerable success among mineralogists and is essentially based on Debye's theory with additional optic-mode contributions determined on the basis of IR and Raman spectra. Although Kieffer's model works surprisingly well in many cases, nevertheless, there are still some assumptions which do not hold in general (see Pilati, Demartin & Gramaccioli, 1993), and for this reason some failure in particular cases is to be expected.

The calculated values for the entropy of monticellite at room temperature are 106.7 and $108.0 J mol^{-1} K^{-1}$ with our force fields nos. (1) and (2), respectively; these values are close to the corresponding experimental value of $108.3 J mol^{-1} K^{-1}$ by Berman (1988). For glaucochroite $CaMnSiO_4$, our calculated value of entropy at room temperature is $137.7 J mol^{-1} K^{-1}$, and there is no experimental counterpart for comparison; here, in view of its antiferromagnetic properties (the Néel temperature is around 9 K, according to Caron *et al.*, 1965) a contribution of $R\ln 6$ ($14.84 J mol^{-1} K^{-1}$) has been added.

A comparison between the results of different force fields can be useful. For instance, as we have seen, our 'older' field [no. (2)] fitted to IR- and Raman-active frequencies of all these minerals of the olivine group gives a reasonable overall agreement with these frequencies; it also behaves quite satisfactorily as far as the entropy values for monticellite and tephroite are concerned, although for the other substances the disagreement between the observed and the calculated values of entropy is more evident (3–6%). However, there is a marked disagreement concerning thermal parameters, especially involving fayalite and tephroite,

and on these grounds the superiority of our force field no. (1) is beyond discussion. This point provides a particularly clear example of the importance of experimental (crystallographic) measurements of a.d.p.'s for checking the validity of empirical force fields, in general.

The only serious disagreement between our calculated thermal parameters (using all our force fields) and the experimental data concerns the O(1) atom in monticellite, where the experimental values of U_{11} and U_{22} are too large. This happens is spite of good agreement for the Raman spectral data and entropy, and substantially good agreement for the corresponding thermal parameters of all the other atoms in the same structure. It should be noticed that (apart from the close similarity in the crystal structure) the atoms in monticellite are the same as those of forsterite, with the only replacement being one half of Mg by Ca. Therefore, a possibility might be that our potentials for the Ca atoms have not been sufficiently calibrated, also in view of the non-availability of IR spectral data; however, our results for andradite $Ca_3Fe_2(SiO_4)_3$, which also contains calcium (Pilati, Demartin & Gramaccioli, 1995), show quite good agreement with the experimental measurements. Another possibility might be connected with the relatively large bond distances of O(1) with Ca (see Table 2): here also, the calibration of the Morse potential might still need additional data.

In such a circumstance, careful refinement of the structures of the iron and manganese equivalents of monticellite, i.e. kirschsteinite $CaFeSiO_4$ and glaucochroite $CaMnSiO_4$, might be helpful. Just for possible comparison with future experimental values, in Table 6 the results of our calculations for glaucochroite are also reported, as well as entropy (see Table 9), although the corresponding experimental data are lacking.

In view of all these circumstances, the present work might be considered in some respects as a first attempt to find a solution to the general problem of establishing empirical potentials which are reliable and transferable, in the absence of more complete experimental data. On the grounds of the good agreement obtained here using the same empirical potentials for various minerals, even considerably different in crystal structure, such as the olivine group and quartz, we would not be surprised if an optimization performed with an adequate supply of good data and considering dependence on more appropriate parameters might provide empirical potentials reproducing the experimental data even beyond the current expectations, with a possibility of being also more general in use.

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Single-Crystal Pulsed Neutron Diffraction of a Highly Hydrous Beryl

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Abstract

The crystal structure of a hydrous beryl with the highest water content on record and coupled with a very high sodium content $(Be_{3.0}(Al_{1.3}Fe_{0.3}Mg_{0.4})Si_{6.0}O_{18}[Na_{0.45}(H_2O)_{0.95}])$ has been refined from single-crystal diffraction data obtained at the ISIS pulsed neutron source in the time-of-flight Laue geometry. The results of the structure analysis allow unambiguous discrimination between the Na cations and the water molecules located in the channel Wyckoff positions 2(*b*) and 2(*a*), respectively, and contribute to the elucidation of the crystal chemical relations among the extra framework species and the cations in the framework sites. The water hydrogens are disordered over multiple sites, with the H—H vectors inclined *ca* 38° with respect to the sixfold symmetry axis, and one O—H vector directed along the axis. The resulting water geometry is different from the orientation of type I and type II water molecules, as reported in the literature from spectroscopic data. The results of the structure refinement based on the neutron diffraction data are compared with those from a refinement based on conventional single-crystal X-ray diffraction data collected on a fragment of the same beryl crystal, and with the results of a combined refinement carried out simultaneously on both data sets.

Introduction

The crystal structure of beryl contains stacks of six-membered rings of Si tetrahedra along [001], cross-linked by Be tetrahedra and Al octahedra. The framework structural channels running along the *c* axis are delimited by the six-membered rings, and often enclose minor amounts of water and alkali cations, the latter needed for charge balance in the Be→Li and Al→Fe,Mg framework substitutions. The crystal chemistry of the water molecules and cations has been extensively studied in the past by spectroscopic and diffraction methods (Wickersheim & Buchanan, 1959, 1965; Vorma, Sahama & Haapala, 1965; Wood & Nassau, 1967, 1968; Gibbs, Breck, & Meagher, 1968; Rehm, 1974; Hawthorne & Černý, 1977; Brown & Mills, 1986; Aurisicchio, Fioravanti, Grubessi & Zanazzi, 1988; Sherriff, Grundy, Hartman, Hawthorne & Černý, 1991). In spite of the effort spent on the