Thermal Parameters for *α*-Quartz: a Lattice-Dynamical Calculation

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Abstract

Using empirical atomic charges and valence force fields, the atomic thermal parameters have been calculated for *α*-quartz (SiO_2) at room temperature. These force fields have been derived from the best fit to the IR- and Raman-active vibrational frequencies, and phonon dispersion curves: in this process, together with quartz, some members of the olivine group, such as forsterite Mg_2SiO_4, monticellite $CaMgSiO_4$, tephroite Mn_2SiO_4 and fayalite Fe_2SiO_4 have been considered. Agreement with the experimental values is good, and good agreement is also obtained for the estimates of thermodynamic functions such as entropy and molar heat. Similarly, as for other silicates and oxides, the zero-point contribution to the vibrational energy amounts to more than 80% at room temperature; the corresponding contribution to thermal parameters is about 30%.

Introduction

The importance of thermal parameters in crystallography has been emphasized previously, both for organic molecular structures (see, for instance, Dunitz, Schomaker & Trueblood, 1988), or inorganic (see, for instance, Ammeter, Bürgi, Gamp, Meyer-Sandrin & Jensen, 1979; Bürgi, 1984; Chandrasekhar & Bürgi, 1984), and also for minerals (see, for instance, Boisen, Gibbs, Downs & D'Arco, 1990; Downs, Gibbs & Boisen, 1990).

For molecular crystals, the physical significance of these crystallographic results and, at the same time, the validity of some models, such as the rigid-body model, have long been confirmed, both on the basis of best fit of experimental data (see, for instance, Cruickshank, 1956*a,b,c*; Schomaker & Trueblood, 1968, 1984; Dunitz & White, 1973; Trueblood, 1978, He & Craven, 1993) and theoretical results (see, for instance, Gramaccioli, 1987, and references therein; Filippini & Gramaccioli, 1989). However, experience in theoretical calculations is not so wide for inorganic substances or minerals, most of which are non-molecular crystals, and especially for structures which are not particularly simple.

The most reliable of these calculations imply lattice-dynamical models following the well known Born–von Karman procedure. This method permits a useful check of empirical force fields used in crystal modelling (Gramaccioli & Pilati, 1992), including their transferability, at least within a group of similar substances. Such calculations may be important, since besides essentially 'crystallographic' information such as thermal parameters, 'spectroscopic' data such as vibrational frequencies and phonon-dispersion curves consistent with the assumed force field can be calculated without extensive difficulty, often permitting a satisfactory interpretation of the experimental data; from these, or even using less sophisticated Debye-like models, values of temperature-dependent thermodynamic functions can also be successfully derived (Kieffer, 1979, 1980, 1982, 1985; Price, Parker & Leslie, 1987; Rao, Chaplot, Choudhury, Ghose, Hastings & Corliss, 1988; Pilati, Bianchi & Gramaccioli, 1990*b*: Pilati, Demartin & Gramaccioli, 1993*a,b*).

Although these procedures are essentially limited to harmonic behaviour, anharmonic models should, nevertheless, still be considered with caution in theoretical calculations of this kind, especially for inorganic crystals whose structure is not disordered and where phase transitions are not considered. This is especially true in view of the substantial difficulties of calculation (which are hardly justified, at least in most cases) since the presumed inadequacy of the

harmonic model might be due, instead, to a lack of well established empirical potentials. This point of view is supported by the generally satisfactory behaviour of the harmonic model even for molecular crystals, where the amplitude of thermal displacement is significantly higher than for inorganic compounds, and good potentials are available. For these reasons we believe that except in certain cases, anharmonicity is not the most important limiting factor of our models.

The indiscriminate use of complex models should be avoided as much as possible, because instead of giving more reliable answers, more sophisticated calculations can be affected by serious errors. For instance, the zero-point motion contribution has been shown to be dominant for oxides and silicates at room temperature (Pilati *et al.*, 1990*b*; Pilati *et al.*, 1993*a,b*) and, because of this quantum effect, classical molecular mechanics routines applied as such may lead to zero thermal displacement at the absolute zero, which is erroneous [for an example of this error, see for, instance, one model given by Matsui (1988) for $MgSiO_3$ perovskite].

For quartz, a first theoretical estimation of anisotropic thermal parameters was provided by Dubrovinskii & Nozik (1989). These authors used the empirical potentials of Urusov, Dubrovinskii & Piloyan (1986), with surprisingly good agreement with the experimental data. Their method does not imply lattice dynamics, and just considers the distribution in space of the atoms around their equilibrium positions as a Boltzmann function of the displacement energy. However, since the various atoms do not move independently of each other, this in general is a dangerous assumption, and might lead to inconsistent results (see also below).

Quartz has long been studied by Raman and infrared spectroscopy, even at different temperatures, including the transition to the β-phase (Scott & Porto, 1967, and references therein; Shapiro, O'Shea & Cummins, 1967; Höchli & Scott, 1971; Bates & Quist, 1972; Etchepare, Merian & Smetankina, 1974; Gervais & Piriou, 1975; Ocaña, Fornes, Garcia-Ramos & Serma, 1987). Lattice-dynamical models were first calculated by Elcombe (1967), and subsequently by Iishi & Yamaguchi (1975), Iishi (1976, 1978), Barron, Huang & Pasternak (1976), Boysen, Dorner, Frey & Grimm (1980), and Iishi, Miura, Shiro & Murata (1983). Phonon dispersion curves were also measured by Elcombe (1967), Dorner, Grimm & Rzany (1980), and Dove, Hagen, Line & Harris (1992). Furthermore, accurate crystal structure refinement, including thermal parameters, has been reported by several authors, *e.g.* Young & Post (1962), LePage & Donnay (1976), or – more recently – by Wright & Lehmann (1981), and Will, Bellotto, Parrish & Hart (1988).

Table 1. *Empirical potentials used here*

Parameters A,B,C for Morse functions: Energy (kJ mol^{-1}) = $A\{\exp[-2B(r-C)] - 2\exp[-B(r-C)]\}$, where r is the distance (Å). Constants K for bending and bending–stretching are given as: $K = A + B$(angle $- 109°\ 28'$).

Force field No.	1	2
		Atomic charge (electrons)
Si	-1.566	-0.891

	Stretching potentials (Morse A,B,C in sequence)	
Si—O	2671.197	1896.949
	0.75610	0.89829
	1.65054	1.61154
O—O (above 5.50 Å)	6.141	4.631
	0.87475	0.73053
	3.68461	3.91225

	Bending potentials (mdyn Å rad^{-2})	
O—Si—O	0.399	0.599
	0.033	0.144
Si—O—Si	0.121	0.169
	0.000	0.000

	Bending–stretching (mdyn rad^{-1})	
O—Si—O/Si—O	-0.190	0.067
	0.012	-0.121

	Stretching–stretching (mdyn Å^{-1})	
Si—O/Si—O	0.276	0.032

At the same time, *ab initio* calculations have been performed at various levels of sophistication on silicate groups to derive several properties, including valence force-field (VFF) parameters (Lasaga & Gibbs, 1987, 1988, 1991; McMillan & Hess, 1990; Kubicki & Sykes, 1993). Empirical force fields have also been extensively used in modelling the crystal structure (Sanders, Leslie & Catlow, 1984; Urusov *et al.*, 1986; Jackson & Gordon, 1988; Lazarev & Mirgodsky, 1991), including phase transformations (Tautz, Heine, Dove & Chen, 1991).

Therefore, following our interest in these calculations and force-field models (Pilati, Bianchi & Gramaccioli, 1990*a,b,c*; Pilati, Demartin & Gramaccioli, 1993*a,b*), we have considered quartz to be especially important in the study of other silicates.

Method of calculation

We have essentially followed the same routines used for forsterite, corundum, bromellite and chrysoberyl (Pilati *et al.*, 1990*a,b,c*; Pilati *et al.*, 1993*a,b*). These routines imply a rigid-ion model, in which almost any kind of valence force-field (VFF) potential can be used, together with a certain value of the atomic charge. The force-field parameters used here are shown in Table 1. The first has been obtained on a best-fit basis of Morse-type potentials to Raman and infrared frequencies on quartz, together with the olivine group minerals (forsterite Mg_2SiO_4, fayalite Fe_2SiO_4, tephroite Mn_2SiO_4, monticellite CaMg-

SiO₄), as measured by Gervais & Piriou (1975), Hofmeister (1987), Chopelas (1991), and Stidham, Bates & Finch (1976) and to the acoustic branches of the phonon-dispersion curves of quartz in the $(hk0)$ plane, as measured by Dorner, Bauer, Jagodzinski, Grimm & Comes (1976), and of forsterite along the three crystal axes, as measured by Ghose, Hastings, Corliss, Rao, Chaplot & Choudhoury (1987). Our second force field has been fitted only to the quartz data.

Results and discussion

The Raman and infrared spectra calculated according to the force fields considered here are shown in Table 2. The agreement with the corresponding experimental values is good (within about 3–4%). There is also a good agreement with the phonon dispersion curves; these are shown in Fig. 1.

The calculated atomic displacement parameters (U values) at room temperature (298 K) are shown in Table 3, together with the corresponding experimental values found in the literature and with the results of the calculations by Dubrovinskii & Nozik (1989). The agreement of our results with the experimental data is quite good, especially with the results reported by LePage & Donnay (1976) and obtained from 'traditional' X-ray diffraction; the values reported by Wright & Lehmann (1981), obtained from neutron diffraction measurements, seem to be somewhat smaller. The results obtained by Will et al. (1988) using profile analysis of synchrotron-radiation high-resolution powder data are also comparable, but their precision is not so good, at least in this respect.

Table 2. *Vibrational spectrum of quartz* (cm^{-1})

Experimental data from Gervais & Piriou (1975).

(1) From force field No. 1 fitting quartz and olivine group.
(2) From force field No. 2 fitting quartz only (see text).

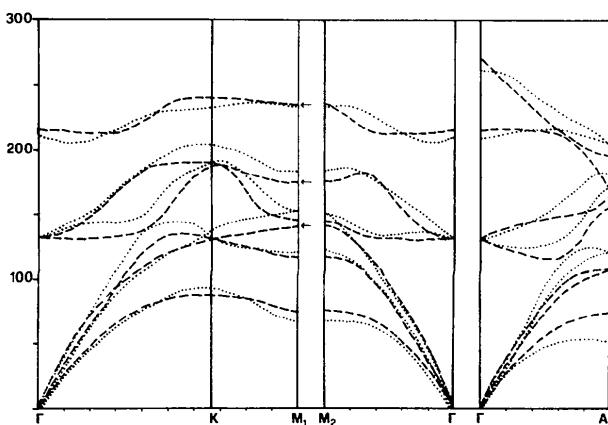|	Observed	Calculated	
		(1)	(2)
E (TO)	128	129	130
	263	268	264
	394	383	384
	450	491	475
	695	692	641
	797	792	775
	1065	1087	1057
	1158	1100	1153
E (LO)	128	129	130
	263	270	265
	402	392	387
	510	523	489
	698	693	643
	810	811	783
	1155	1099	1153
	1226	1152	1169
A1	205	212	206
	354	362	362
	464	526	503
	1081	1068	1131
A2 (TO)	364	354	347
	495	518	495
	777	748	755
	1071	1090	1124
A2 (LO)	387	375	361
	552	548	507
	790	760	761
	1229	1156	1140

Fig. 1. Observed (dotted) and calculated phonon-dispersion curves (dashed) for quartz (values in cm⁻¹). The observed curves are schematic and represent a reasonable interpolation of the observed values by Dorner et al. (1976, 1980) or Elcombe (1967). The modes associated with the symmetry representation T_1 are indicated by an arrow.

The agreement of Dubrozinskii & Nozik's (hereafter referred to as D&N) results is quite good, surprisingly enough. Their model cannot be expected to give a good general performance, mainly because in most cases the atomic distribution in space is strongly correlated. For instance, the atomic displacement can be quite large even along a strong bond, provided the bonded atoms are part of the same unit which moves as a rigid body, hindered only by a weaker force field, and examples of this are given by a number of molecular crystals. Therefore, a model neglecting correlated motion should be expected, in general, to give substantially smaller atomic displacement parameters than the corresponding experimental values.

Another difficulty of the model proposed by D&N apparently concerns zero-point effects, which are important (see below). In their 'classical' expression the mean-square displacement is zero at 0 K (see their equation 9), and consequently the zero-point motion has not been accounted for. Since both these errors should work in the same direction, a possible explanation of D&N's success lies in the choice of potentials, which are probably too soft with respect

Table 3. *Thermal parameters for quartz* ($\times 10^4$) *at room temperature* (298 K)

The temperature factor is in the form: $\exp - 2\pi^2(U_{11}ha^{*2} + \ldots\ldots + 2U_{23}klb^*c^*)$.

Atom		11	12	13	22	23	33
Si	obs (L&D)	66 (1)	26 (1)	−1 (1)	51 (1)	−3 (1)	60 (1)
	obs (W&L)	56 (2)	19 (1)	−3 (1)	39 (2)	−6 (2)	52 (2)
	obs (WBPH)	59 (7)	17 (5)	−20 (10)	30 (10)	−10 (5)	43 (8)
	calc (1)	69	26	−1	52	−1	60
	calc (2)	71	26	−1	53	−1	65
	calc (D&N)	64	28	−1	56	−1	59
O	obs (L&D)	156 (4)	92 (3)	−29 (3)	115 (3)	−46 (2)	119 (3)
	obs (W&L)	137 (2)	78 (1)	−30 (1)	93 (2)	−48 (1)	109 (1)
	obs (WBPH)	80 (20)	120 (30)	−20 (30)	90 (30)	0 (208)	90 (20)
	calc (1)	140	79	−27	106	−40	112
	calc (2)	150	88	−32	113	−44	118
	calc (D&N)	163	99	−28	129	−51	130

Notes: (1) All-Morse fitting quartz and olivine group. (2) All-Morse fitting quartz only. (L&D) observed data (X-ray) by LePage & Donnay (1976). (W&L) observed data (neutron diffraction) by Wright & Lehmann (1981). (WBPH) observed data (synchrotron radiation on powder) by Will *et al.* (1988). (D&N) calculated values by Dubrovinskii & Nozik (1989).

Table 4. *Correlation tensors* $[U_{ij} = \langle u_i u_j^T \rangle$ ($\times 10^4$)] *at* 298 K *between bonded atoms, according to our potential No.* 1

The second index is relative to the second atom, and 1, 2 or 3 indicate the component along the Cartesian axis *x*, *y* or *z*.

	11	21	31	12	22	32	13	23	33
Si—O	49	−4	−8	−6	47	3	−6	1	37
Si—O*	50	−5	−2	−10	38	1	−3	3	48

Bond distances (Å)		
	Uncorrected†	Corrected
Si—O	1.607 (1)	1.614
Si—O*	1.611 (1)	1.618

* Symmetry transformation (for 0:) $-y$; $x + y$; $2/3 + z$.
† From LePage & Donnay (1976).

Table 5. *Values of thermodynamic functions at* 298 K

	Observed	Calculated*	
		(1)	(2)
Entropy (J mol^{-1} K)	41.46 (0.2)† 41.33‡	41.72	42.32
Heat capacity c_p (J mol^{-1} K)	44.59 (0.09)§ 44.42 (0.2)¶ 44.47‡	44.11	44.70
Zero-point energy (J mol^{-1})		30.27	29.98
Total vibrational energy at 298 K (J mol^{-1})		37.13	36.94

* (1) and (2) specify the force field used (see Table 1).
† Recommended value in CODATA (1976); see also Berman (1988).
‡ Helgeson (1978), Table 2.
§ Hemingway (1987).
¶ Kuskov & Fabrichnaya (1987), Table 2.

to vibrational problems, and, therefore, the errors are balanced in some way.

The correlation tensors $U_{ij} = \langle u_i u_j^T \rangle$ at room temperature are shown in Table 4; from these correlation tensors, the general bond-length correction becomes almost exactly + 0.007 Å at room temperature.

The calculated values of thermodynamic functions such as entropy, *S*, and the molar heat capacity are shown in Table 5, together with some of the most reliable corresponding experimental data. Since measurements of the heat capacity at constant pressure (c_p) are usually reported, instead of the heat capacity at constant volume (c_v), which is directly obtained from the density of states, the calculated value of c_p has been obtained starting from c_v and using the relationship of the difference ($c_p - c_v$) to the bulk modulus (K) and thermal expansion coefficient (α). For this purpose, the values reported by Kuskov & Fabrichnaya (1987) in their Table 2 have been used.

Even for thermodynamic functions, the agreement with the experimental data is quite satisfactory, the

difference being of the order of magnitude of the standard deviation and the calorimetric values are reproduced to within about 0.5%. Also, in this case, our field specifically fitted to quartz only (No. 2) does not seem to give a better agreement with the experimental data than the other field (No. 1) derived in great part from the olivine group minerals. This can be taken as a good indication for the existence of a substantially transferable potential (Pilati *et al.*, 1994).

As for the oxides and silicates we have studied so far (Pilati *et al.*, 1990*b*; Pilati *et al.*, 1993*a,b*), here the zero-point effects are particularly important. For instance, at 0 K, the vibrational energy and thermal parameters are about 80 and 33% of the values at room temperature, respectively.

Our calculations were not extended to temperatures higher (or lower) than 298 K. For this structure we have noticed that even for minor shifts of the

atomic coordinates there is a strong variation in the calculated frequencies, and no accurate crystal data on α-quartz at various temperatures seem to be available as yet in the literature (with the exception of unit-cell measurements and considerable work dealing with phase transformations). All this has forced us to restrict this study to room temperature only, with a strong emphasis on the need for further crystallographic measurements on this substance under various conditions.

In conclusion, it seems that essentially transferable empirical potentials can satisfactorily interpret the vibrational behaviour of quartz, including thermal parameters and temperature-dependent thermodynamic functions. In this respect, further accurate measurements of structure parameters of quartz, including the U values at different temperatures, as well as of additional phonon-dispersion curves, would be quite welcome.

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Inter-Relationship of Octahedral Geometry, Polyhedral Volume Ratio and Ferroelectric Properties in Rhombohedral Perovskites

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Abstract

A unifying, quantitative analytical framework has been developed for rhombohedral perovskite structures, ABO_3. Three principal parameters are defined: polyhedral volume ratio, V_A/V_B, mean octahedral tilt angle, $\langle\omega\rangle$, and octahedral distortion, Δs. The first two of these parameters are directly related through the equation $V_A/V_B = 6K\cos^2\langle\omega\rangle - 1$, with K practically invariant between all crystal structures. The four permutations of zero or non-zero $\langle\omega\rangle$ with zero or non-zero Δs are related to the four space groups in which rhombohedral perovskites crystallize, $R3m$, $R3c$, $R\bar{3}m$ and $R\bar{3}c$. The most general space group is $R3c$, which can accommodate non-zero values of both $\langle\omega\rangle$ and Δs. The structural driving force for non-zero Δs values (*i.e.* octahedral distortion) is examined by the bond-valence method, with the rationalization that octahedral distortions provide a mechanism for B-ion displacements which are parallel to one another and to the hexagonal z axis. Calculations of electrostatic energy further reveal the extra stabilization to be obtained by the adoption of electric dipole moments and parallel A- and B-ion displacements. It is these displacements which give rise to the ferroelectric properties of rhombohedral perovskites. The analysis is applied to the PZT system ($PbZrO_3$–$PbTiO_3$) and to the $PbZrO_3$–$BaZrO_3$ and $PbZrO_3$–$SrZrO_3$ systems. The influence of chemical composition on the relative stabilities of competing rhombohedral, orthorhombic and tetragonal phases is discussed, as is the physical basis of the morphotropic phase boundary in PZT. A method is also defined of predicting the temperatures at which the rhombohedral low-temperature phase in PZT transforms to the rhombohedral high-temperature phase, for a range of compositions.

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Introduction

The geometrical relationships governing the structures of rhombohedral perovskites, ABO_3, have been the focus of previous work (Michel, Moreau & James, 1971; Megaw & Darlington, 1975). The structural feature of most interest is the possible occurrence of BO_6 octahedral tilting, since this is thought to influence the ferroelectric, piezoelectric and electro-optic properties which can be shown by this class of materials. With the assumption of regular BO_6 octahedra, Michel *et al.* derived a relationship between hexagonal axial ratio c/a, octahedral tilt angle ω and rhombohedral cell angle α. A further relationship was derived, linking c/a with the positional parameter x of the anion $[x, 0, \frac{1}{4}]$ in position 18(*e*) ($R3c$, hexagonal). Megaw & Darlington subsequently proposed a more general parametrization, accommodating octahedral distortions and cation displacements explicitly. They considered the inter-relationship between A-cation size, tilt angle, octahedron strain, and A- and B-cation displacements, and concluded that 'a single 'explanation' will not suffice for compounds so varied as the rhombohedral perovskites, in spite of their similar geometry.'

In this paper, however, it is shown that a single 'explanation' can indeed be given of the structures of rhombohedral perovskites. In particular, the ratio of the polyhedral volumes of the A- and B-cation polyhedra, V_A/V_B, can be correlated directly with octahedral tilt angle, ω. Whereas Megaw & Darlington failed to find a universal relationship between cation size† and tilt angle, such a relationship is derived in this work, where V_A/V_B is expressed as a function of ω. The effect of octahedral

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† Megaw & Darlington (1975) used the parameter $(r_A + r_o)/l$ as a measure of 'ionic size', where r_A and r_o are the radii of A cations and oxygen anions, and l is the octahedron edge length.