

Transferability of Empirical Force Fields in Silicates: Lattice-Dynamical Evaluation of Atomic Displacement Parameters and Thermodynamic Properties for the Al_2OSiO_4 Polymorphs

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Abstract

A Born–von Karman rigid-ion lattice-dynamical model, using empirical atomic charges and valence force fields derived from the best fit to the vibrational frequencies of a group of silicates and oxides, has been applied to andalusite, kyanite and sillimanite, the three naturally occurring Al_2OSiO_4 polymorphs. For andalusite there is good agreement with the atomic anisotropic displacement parameters (ADP's) derived from accurate crystal structure refinement at different temperatures and with the values of thermodynamic functions, such as the specific heat and entropy. For kyanite, our calculations are successful in reproducing the values of thermodynamic functions, but not the ADP's, almost certainly due to the poor quality of the crystals used in the structure determination. For sillimanite, imaginary frequencies are obtained in a region of the Brillouin zone: such an inadequacy might be ascribed to the presence of four-fold coordinated Al, whose properties are considerably different from those of higher-coordinated Al present in andalusite and kyanite.

1. Introduction

Following our interest in the field, which initially started from molecular crystals (see, for instance, Gramaccioli, 1987, 1992; Gramaccioli & Pilati, 1992, and references therein), and also in line with a recent recommendation (Kuhs, 1992) for 'a more frequent comparison of theoretical calculations and experimental determinations of generalized ADP's', we have tried to extend our harmonic lattice-dynamical calculations of thermal parameters to minerals, initially considering some oxides such as corundum, quartz, chrysoberyl and bromellite, and silicates such as the olivine group, garnets and diopside [Pilati, Bianchi & Gramaccioli, 1990c: from hereon PBG90c; Pilati, Demartin & Gramaccioli, 1993 (PDG93); Pilati, Demartin, Cariati, Bruni & Gramaccioli, 1993; Pilati, Demartin & Gramaccioli, 1994 (PDG94); Pilati, Demartin & Gramaccioli, 1995

(PDG95); Pilati, Demartin & Gramaccioli, 1996a,b (PDG96a,b)].

On one hand, our results have emphasized the physical meaning of the accurate crystallographic determination of these parameters and, on the other hand, the possibility of wide and successful application of rigid-ion lattice-dynamical models to minerals using transferable empirical potentials has been confirmed. These conclusions are in agreement with several authors, such as for instance Rao, Chaplot, Choudhury, Ghose, Hastings & Corliss (1988); Dove, Winkler, Leslie, Harris & Salje (1992); Catti, Pavese & Price (1993); Kihara (1993); Ghose, Choudhury, Chaplot, Pal Chowdury & Sharma (1994) *etc.* In view of their actual physical meaning, the experimental estimates of ADP's can be considered as a source of precious information concerning the specific vibrational behaviour of *every atom* in the various directions *over the whole Brillouin zone*. Another interesting result of our calculations concerns the importance of zero-point motion, which in most cases is of the order of one third to one half of the total at room temperature.

In view of a further extension of our calculations to more complex silicates, our attention was drawn to the naturally occurring phases of the aluminium silicate Al_2OSiO_4 , *i.e.* to andalusite, kyanite and sillimanite, which are of considerable mineralogical and petrological interest. As a first example, andalusite seemed to be particularly useful, because its structure is relatively simple; good (and pure) natural crystals of this substance are fairly readily available and there are a number of reliable experimental data available for comparison. These data include crystal structure determinations, even under different physico-chemical conditions (Burnham & Buerger, 1961; Ralph, Finger, Hazen & Ghose, 1984; Winter & Ghose, 1979: here onwards WG), Raman and IR spectra (Iishi, Salje & Werneke, 1979, here onwards ISW; Salje & Werneke, 1982, here onwards SW; Winkler & Buehrer, 1990, here onwards WB), phonon dispersion curves (WB) and thermodynamic functions (SW; Robie & Hemingway, 1984; Salje,

1986). Apart from experimental work, there are also lattice-dynamical calculations for andalusite, performed by a number of authors using different potentials (ISW; SW; WB; Winkler, Dove & Leslie, 1991); therefore, a comparison between the results of various authors and our own was also considered to be useful and interesting.

2. Experimental

For comparison with our calculations, the possibility of using accurately determined experimental sets of ADP's, in addition to those already available in the literature, was considered. Accordingly, a crystal of gem-grade andalusite from Val Chiavenna measuring $ca\ 0.11 \times 0.15 \times 0.17$ mm was mounted on a Nonius CAD-4 diffractometer, using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The crystal was found to be essentially pure by examining it in an Hitachi S2400 SEM (scanning-electron microscope) equipped with an energy-dispersion spectrometer (EDS). Andalusite is orthorhombic, with space group $Pn\bar{m}$. The unit-cell parameters at room temperature are $a = 7.7992$ (6), $b = 7.9050$ (6), $c = 5.5591$ (5) Å, derived from a least-squares fit of 25 independent reflections with θ ranging from 16.9 to 17.3°. For crystal structure refinement, reflections up to a θ value of 40° were collected. A total of 2388 diffracted intensities were collected at room temperature (295 ± 2 K) with variable scan speed (maximum scan time for each reflection: 60 s) by exploring the reciprocal space with $-14 < h < 14$, $0 < k < 14$ and $0 < l < 10$. The diffracted intensities were corrected for Lorentz-polarization and absorption (Walker & Stuart, 1983): the transmission factors were in the range 0.92–1.06. After averaging the symmetry-related data, which had an agreement of 1.3% based on F_o , 1135 independent reflections were obtained. Of these, 875 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 scattering factors). Scattering factors for neutral atoms and anomalous-dispersion corrections for scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The refinement of the structure was carried out by full-matrix least-squares, using the *SDP* crystallographic programs (B. A. Frenz & Associates Inc., 1983), and minimizing the function $\sum w(|F_o| - |F_c|)^2$. The final weights were assigned equal to $1/\sigma^2(F) = 4I/\sigma^2(I)$; the variance of each $\sigma^2(I)$ reflection 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. The estimates of ADP's can be strongly affected by various effects, such as absorption, secondary extinction and

Table 1. *Positional parameters for andalusite and their e.s.d.'s*

	x	y	z
Si	0.24606 (3)	0.25217 (3)	0.0
Al1	0.0	0.0	0.24196 (4)
Al2	0.37054 (3)	0.13900 (3)	1/2
O(A)	0.42326 (8)	0.36293 (7)	1/2
O(B)	0.42438 (8)	0.36293 (7)	0.0
O(C)	0.10280 (7)	0.40022 (7)	0.0
O(D)	0.23064 (5)	0.13397 (5)	0.23948 (8)

Parameters without e.s.d.'s are symmetry fixed.

truncation errors in integrated intensity measurements [see, for example, Denne (1977) and Eisenstein (1979)]. Accordingly, in the final refinement the coefficient g of secondary extinction was introduced (Stout & Jensen, 1968). The crystal structure was separately refined using: (a) data uncorrected for absorption; (b) data corrected using the ψ -scan method; (c) data corrected by the method of Walker & Stuart (1983). For all atoms the differences between the corresponding ADP's of the three sets were less than 3σ and for this reason absorption was confirmed to be almost negligible in this particular case; similarly, extinction ($g = 8.9 \times 10^{-6}$) is not particularly high and it has practically no influence on the values of the ADP's. For use in structure refinement, the third set of data was preferred, because it corresponded to the lowest R in merging the equivalent reflections. The final values of the R index equals $\sum ||F_o| - |F_c|| / \sum |F_o|$ and of the corresponding weighted index, $wR = [\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}$, are 0.014 and 0.018, respectively. The atomic coordinates are reported in Table 1.* In the final difference synthesis, no peak exceeding $0.4 e \text{ \AA}^{-3}$ was found. The final value of the goodness-of-fit was found to be 0.938. The ratio $\Sigma F_o / \Sigma F_c$ as a function of θ , as evaluated by considering groups of 100 reflections, varies from 0.980 to 1.013, showing no evident trend; this indicates that truncation errors are not important here.

For kyanite we also tried to collect a new set of experimental data. However, in spite of repeated attempts on selected material from different occurrences (Brazil, Pizzo Forno in Canton Ticino), we were not able to obtain a crystal good enough for our requirements, since the mosaic spread of the reflections was too large; this inconvenience was due to the almost plastic behaviour of the material, which prevented adequate cutting to reduce the size. This phenomenon is identical to that encountered by other authors (see, for instance, WG) and is very probably the reason why the calculated ADP's for kyanite strongly disagree with the corresponding experimental estimates (see below).

* Lists of geometric parameters and structure factors have been deposited with the IUCr (Reference: CR0515). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

3. Procedure of calculation

Our calculations proceed according to a classic rigid-ion lattice-dynamical model, extended to the whole Brillouin zone (for details, see for instance PBG90c; Pilati, Bianchi & Gramaccioli, 1990a,b: from hereon PBG90a,b). Following a well established scheme, from the second derivatives of the potential energy with respect to the positional coordinates of all the atoms in the primitive unit cell [multiplied by $\exp(2\pi i\mathbf{q}\cdot\mathbf{r})$, where \mathbf{q} is the wavevector and \mathbf{r} is the vector distance between two interacting atoms], dynamical matrices are built (one for each value of \mathbf{q}). The square roots of the eigenvalues of these matrices correspond to the vibrational frequencies $\nu_i(\mathbf{q})$ of the various normal modes, whereas the components of the eigenvectors characterize the shift and the phase of each particular atom in the normal mode.

From these calculated vibrational frequencies extended to all the Brillouin zones the phonon density-of-states can be evaluated; then, on applying statistical thermodynamics *via* the vibrational partition function, the values of thermodynamic functions such as the vibrational energy E_v , entropy S or the specific heat at constant volume C_v can be easily obtained at different temperatures; from the average energy of each vibrational mode $E_i(\mathbf{q})$ and the eigenvectors of the dynamical matrices $\mathbf{D}(\mathbf{q})$, ADP's (as \mathbf{U} 's) can also be readily calculated [see, for instance, Willis & Pryor (1975)]. In particular, the following expressions are important for our purposes

$$E_i(\mathbf{q}) = h\nu_i(\mathbf{q}) \left(\frac{1}{2} + \{ \exp[h\nu_i(\mathbf{q})/kT] - 1 \}^{-1} \right) \quad (1)$$

$$E_v = \sum_{i,\mathbf{q}} E_i(\mathbf{q}) \quad (2)$$

and also

$$\mathbf{U}(p) = (Nm_p)^{-1} \sum_{i,\mathbf{q}} E_i(\mathbf{q}) [2\pi\nu_i(\mathbf{q})]^{-2} \mathbf{e}(p|i\mathbf{q}) [\mathbf{e}^*(p|i\mathbf{q})]' \quad (3)$$

$$S = E_v/T - 3R \sum_{i,\mathbf{q}} g_i(\mathbf{q}) \ln[1 - \exp(h\nu_i(\mathbf{q})/kT)] \Delta\nu_i(\mathbf{q}) \quad (4)$$

$$C_v = \partial E_v / \partial T, \quad (5)$$

where $E_i(\mathbf{q})$ is the average energy for a certain $i(\mathbf{q})$ mode relative to a certain value of the wavevector \mathbf{q} , which is also the contribution of the mode to the total vibrational energy, $\mathbf{U}(p)$ is the ADP tensor relative to the atom p , h and k are the Planck and Boltzmann constants, respectively, T is the absolute temperature, N is Avogadro's number and $\mathbf{e}(p|i\mathbf{q})$ are the mass-adjusted polarization vectors of the atom in the unit cell, which are part of the eigenvectors of $\mathbf{D}(\mathbf{q})$. Here $g_i(\mathbf{q})$ is a phonon density-of-states function, normalized so that $\sum_{i,\mathbf{q}} g_i(\mathbf{q}) \Delta\nu_i(\mathbf{q}) = 1$.

Sometimes the same density-of-states is used for a whole range of different temperatures. Following this approximation, apart from a very notable reduction of the computing time, there is no need to use atomic

coordinates and unit-cell parameters taken from a series of different sets of crystal structure data, each pertinent to certain physico-chemical conditions (such as temperature and pressure). The results in Tables 5–7 have been obtained in this way, starting from room-temperature data, and corrections to the calculated values of thermodynamic functions have been performed as explained below.

On comparing expressions (1)–(5), it is clear that, for instance, if the vibrational energy is calculated too low, other thermodynamic functions such as S and C_v and the estimates of the \mathbf{U} 's would also be too low. Instead, if the frequencies are calculated too low, the functions E_v , S , C_v and the \mathbf{U} 's would be estimated too high. This observation is fundamental for our purposes (see below), since it provides a mutual check between different physical properties.

An important possibility is also that of deriving or optimizing the empirical potentials, so that the best fit to some particular experimental data (such as, for instance, the vibrational frequencies of a group of minerals) is obtained. For this purpose, the program VA04A (QCPE program number 60; Powell, 1965) has been employed. Most of the experimental data used in the optimization process are Raman and IR spectra; whenever they are available, such as, for example, for quartz, forsterite and andalusite, the lowest branches of the phonon dispersion curves could also be considered. Since the rigid-ion model is not fully adequate in reproducing the highest frequencies (whose contribution to the ADP's and thermodynamic functions is, however, negligible), an appropriate weight (inversely proportional to the square) was assigned to each experimental frequency.

For the lattice-dynamical calculations, a computing program has been written entirely by us; our routines include a number of new methods, involving, for example, the evaluation of Coulombic lattice sums or the uneven sampling of the Brillouin zone to obtain a fast convergence (Filippini, Gramaccioli, Simonetta & Suffritti, 1976; PBG90a,b). The program input essentially consists of experimental crystallographic data (unit-cell parameters and atomic fractional coordinates, symmetry space-group operations) and energy-determining information, such as the atomic charge, type of valence force-field (VFF) empirical potential and its parameters.

Concerning the nature of the empirical potentials, for atom–atom interactions we presently prefer Morse functions instead of '6-exp' functions and/or fixed stretching constants, as we used in our earlier works. The advantage of these Morse potentials was already evident for quartz, where the agreement with the experimental vibrational frequencies was definitely improved (PDG94). In our latest sets of potentials, bending constants of all metal-centred bond angles which had not been considered previously were also introduced, improving the general fit; as a result, for some minerals, such as grossular

Table 2. *Empirical potentials used here*

Atomic charge (electrons)			
Si		-1.418	
Al		-1.482	
Ca		-1.337	
O	Calculated by difference to respect charge balance		
Stretching potentials (Morse functions)			
	<i>A</i> (kJ mol ⁻¹)	<i>B</i> (Å ⁻¹)	<i>C</i> (Å)
Si—O	2798.030	0.75624	1.64173
Al—O	264.3066	1.37406	1.90997
O—O (<5.50 Å)	5.97077	0.85146	3.67660
Bending potentials (mdyn Å rad ⁻²)			
	<i>A</i>	<i>B</i>	<i>C</i>
O—Si—O	0.12569	-0.62573	1.11716
O—Al—O	0.48290	0.65945	0.04747
Al—O—Al	0.12007		
Al—O—Si	0.18120		
Si—O—Si	0.13883		
Bending-stretching (mdyn rad ⁻¹)			
	<i>A</i>	<i>B</i>	θ_0
O—Si—O/Si—O	0.10091	-0.05480	109.47
O—Al—O/Al—O	0.14044	-0.00149	90.0
Stretching-stretching (mdyn Å ⁻¹)			
Si—O/Si—O	0.11538		
Al—O/Al—O	0.04744		

Parameters *A*, *B* and *C* for Morse functions as: Energy = $A[\exp\{-2B(r-C)\} - 2\exp\{-B(r-C)\}]$, where *r* is the distance. Constants *K* for bending as: $K = A + B\cos\theta + C\cos^2\theta$, where θ is the angle. When *B* and/or *C* are not given, they are zero. For bending-stretching $K = A + B(\theta - \theta_0)$. The potentials have been derived from best fit to quartz, bromellite (BeO), chrysoberyl (Al₂BeO₄), corundum (α -Al₂O₃), members of the olivine group (forsterite α -Mg₂SiO₄, tephroite Mn₂SiO₄, monticellite CaMgSiO₄, fayalite Fe₂SiO₄), andalusite and some garnets (pyrope Mg₃Al₂Si₃O₁₂ and andradite Ca₃Fe₂Si₃O₁₂): see PDG94, PDG95.

and diopside, a very good agreement with the observed vibrational spectra was obtained, although no experimental data actually to the mineral were considered in deriving the potentials. A more detailed discussion about these arguments is given in PDG95 and PDG96*a,b*.

Owing to the basic difference between O—X—O angles of almost 180 or 90°, as they are found in octahedra, and also to the notable deformation of the oxygen polyhedra around the Al atoms in andalusite, which contains both six- and fivefold coordinated Al, bond-bending potentials strongly depend on the value of the angle which has been introduced (see Table 2).

To evaluate thermodynamic functions such as the specific heat C_v and the entropy S , the vibrational partition function and its derivatives are derived from the phonon density-of-states as obtained from lattice dynamics. Since the specific heat is usually measured at constant pressure (C_p) and not at constant volume (C_v), the well known thermodynamic relationship between C_p and C_v is used

$$C_p - C_v = \alpha^2 TVK_T, \quad (6)$$

where α is the volume expansion coefficient, V is the volume of the substance and K_T is the bulk modulus. Since the volume expansion is linked to anharmonicity, the above expression is sometimes regarded as a partial correction for anharmonic behaviour. If C_v is evaluated using crystal structure data taken at a different temperature (such as, for instance, those at room conditions in the case of elaboration of thermodynamic data for a whole temperature range using the same density of states), then the calculated values should be corrected; however, the correction is usually negligible unless there is a notable variation of the thermal expansion coefficient or of the bulk modulus [see expression (10) and discussion below].

The problem of evaluation of entropy S from the partition function and the density of states is also delicate. Using the same procedure we have proposed for diopside (PGD96*b*) the following path is considered

$$\begin{aligned} (1) \quad T = 0 \text{ K}, V = V_0 &\rightarrow (2) \quad T = 0 \text{ K}, V = V_{298} \rightarrow \\ (3) \quad T = 298 \text{ K}, V = V_{298} &\rightarrow (4) \quad T = T_i, V = V_i, \end{aligned}$$

where T and V are the temperature and the volume of the substance; V_0 is the equilibrium volume at 0 K at a given pressure (say, for instance, 1 atm); V_{298} is the equilibrium volume at 298 K and 1 atm; V_i is the volume at temperature T_i and 1 atm pressure. Since entropy is a function of state, its variation is independent of the method chosen to change conditions. It will be

$$\begin{aligned} S(4) - S(1) &= S(2) - S(1) + S(3) - S(2) + S(4) - S(3) \\ &= S(2) - S(1) + \int_0^{298} C_v(298)/TdT \\ &\quad + \int_{298}^{T_i} C_p/TdT, \end{aligned} \quad (7)$$

where the last two steps are performed at constant volume (V_{298}) or at constant pressure (1 atm), respectively, and $C_v(298)$ indicates the value of C_v at temperature T , but with volume = V_{298} . Owing to the third law of thermodynamics $S(1)$ and $S(2)$ are both zero (assuming there is no disorder and the crystal is pure). Therefore, equation (7) can be rewritten as

$$\begin{aligned} S(4) = S(T_i, V_i) &= \int_0^{T_i} C_v(298)/TdT \\ &\quad + \int_{298}^{T_i} (C_p - C_v)/TdT \\ &\quad + \int_{298}^{T_i} [C_v - C_v(298)]/TdT. \end{aligned} \quad (8)$$

In expression (8) shown above the first term corresponds to the lattice-dynamical estimate of S at temperature T_i , obtained using the volume (in practice, the

crystal structure data) at 298 K. The second term, taking account of (6), can be written as

$$\int_{298}^{T_i} (C_p - C_v)/TdT = \int_{298}^{T_i} \alpha^2 V K_T dT. \quad (9)$$

It should be noted besides that V , α and K_T are usually derived from crystallographic measurements and this derivation is a good example of applying crystallography to thermodynamics. The third term in (8) accounts for the variation of the specific heat C_v with respect to the volume. However, according to classic thermodynamics, we have

$$(\partial C_v / \partial V)_T = T[\partial(\alpha K_T) / \partial T]_v. \quad (10)$$

Therefore, if the product of the expansion coefficient and the bulk modulus may be regarded as temperature-independent, C_v becomes volume-independent and consequently there would be no difference between C_v and $C_v(298)$. Accordingly, since even the volume V and α are not subjected to extensive variations with temperature, we have

$$\begin{aligned} S(T_i) &= \int_0^{T_i} C_v(298)/TdT + \int_{298}^{T_i} (C_p - C_v)/TdT \\ &\simeq \int_0^{T_i} C_v(298)/TdT + \alpha^2 V_{298} K_T (T - 298). \end{aligned} \quad (11)$$

If the temperature dependence of α and K_T is known, as it is in several cases, then not only a better estimate of expression (11) can be obtained, but in principle the third term in expression (8) might also be calculated. For instance, assuming a linear dependence of the variables upon volume and temperature, from expression (10) we have

$$\begin{aligned} C_v - C_v(298) &\simeq T[\partial(\alpha K_T) / \partial T](V - V_{298}) \\ &= T(\alpha V)_{298} [\partial(\alpha K_T) / \partial T](T - 298), \end{aligned}$$

where $(\alpha V)_{298}$ is the value of the product αV at 298 K. Therefore

$$\begin{aligned} \int_{298}^{T_i} [C_v - C_v(298)]/TdT &\simeq \frac{1}{2}(\alpha V)_{298} \\ &\times [\partial(\alpha K_T) / \partial T](T - 298)^2. \end{aligned} \quad (12)$$

If $T_i = 298$ K the last integral in (11) is zero, as well as expression (12), and in this case the calculated lattice-dynamical value of entropy, which corresponds to the first term in (8) or (11), is indeed *exactly* equivalent to $\int_0^{T_i} C_p/TdT$. The same happens for any temperature corresponding to that of the crystal structure used in the lattice-dynamical model. In any case, the above described procedure [equation (11)] is a reasonable approximation which may be particularly useful when

no data except those at room temperature are available and only a certain range of temperatures is considered, where the values of the volume expansion coefficient α and the bulk modulus remain reasonably close to the corresponding values at 298 K. In some cases, however, especially at low temperature, α is far from being constant (for instance, at $T = 0$ K according to the third law $\alpha = 0$) and in these cases an accurate evaluation of the integrals in (9) and (12) should be properly considered.

A delicate point in this procedure is the assumption that the vibrational spectra are temperature-independent at constant volume, *i.e.* (see also above) on these grounds for these purposes the unit-cell data and their variation with temperature should be more important than a detailed knowledge of atomic coordinates. This assumption seems to be reasonable, since at constant volume the interatomic distances and bond angles which characterize the values of the frequencies through the force field are not liable to significant change on varying temperature. In any case, on performing calculations using accurate crystal data pertinent to certain physical conditions (temperature and pressure), then $S(2)$ is always zero, independent of the crystal structure data (both unit-cell parameters and atomic coordinates), and the lattice-dynamical estimate for entropy corresponding to the first term of (8) *for these conditions only* needs no further correction.

As we have seen, at least some approximate corrections should be used for entropy or thermodynamic functions in general when the crystal structure used as a model does not correspond to the same temperature for which the calculations are performed, whereas no simple correction of this kind seems to be possible for the ADP's. However, since the experimental values of ADP's are rarely very accurate and, in any case, in this respect they are never comparable to the values of thermodynamic functions nor are they directly linked to important physico-chemical properties of the materials, here, no need to introduce more sophisticated corrections is envisaged.

Furthermore, here, no attempt has been made to derive from the empirical potentials the equilibrium conformation as a minimum of the free energy (or at least of the energy) under different conditions. Such calculations have actually been carried out by several authors (Price & Parker, 1988; Catlow, 1988; Dove, 1989; Winkler, Dove & Leslie, 1991; WB; Dove, Winkler, Leslie, Harris & Salje, 1992); however, our present potentials have been accurately refined only with respect to the second derivatives and the possibility of extending them also to account for first derivatives is actually being considered. Our philosophy is that such an extension should be mainly regarded as finding appropriate integration constants for our present expressions and, therefore, no variation in second derivatives and their consequent applications (such as the results in this paper) should

follow; now we can only assume that the potentials (whatever they are) should correspond to the observed structure, as a free-energy minimum.

Although such an assumption might appear as rather restrictive, it, however, does save a very considerable amount of computing, at present the only scope of our work being the derivation of vibrational frequencies and their applications, starting from crystal structure data as unit-cell parameters, symmetry operations and atomic coordinates, omitting any *a priori* modelling. If successful, even such a restrictive application might properly emphasize the importance of accurate crystallographic work for thermodynamic and spectroscopic applications in various disciplines.

4. Discussion

The results are shown in Tables 3–8. Agreement with the experimental Raman and IR spectral data is especially good for the medium–low frequencies (usually within 10 cm^{-1}), where the experimental errors are less pronounced than for the lowest ones and where the rigid-ion model is reasonable, as opposed to the highest frequencies. Probably also owing to experimental difficulties, the agreement is consistently better for the Raman data with respect to the IR. On the whole, the interpretation of the frequencies in the spectra as fundamental given by the other authors who studied the problem (ISW; SW; WB) is essentially confirmed, although our calculations on the whole give a better agreement with the experimental data; the calculated values by WB being generally too low and those by ISW rather too high (with the only exception of the B_{3g} - and most of the B_{2g} -modes, where the agreement is very good with ISW's calculations). Due to the strong connection with thermodynamic functions and ADP's [see above, or also, for instance, Willis & Pryor (1975)], the good agreement of our calculated values for such data (see below) gives a substantial proof in favour of our interpretation, since if the frequencies were consistently too low or too high (especially the lowest ones, which are the most important contributors), then the calculated values of entropy and of the ADP's would result notably too high or too low, respectively. In spite of a general good agreement, there are a few exceptions: for instance, according to our model there should be an A_g -frequency at *ca* 430 cm^{-1} , whereas the observed one at 834 cm^{-1} should not be a fundamental; similarly, there should be an additional low-frequency B_{3g} -mode around 100 cm^{-1} and another B_{3u} -mode around 200 cm^{-1} (in agreement with the calculations of the other authors) *etc.*; rather than indicating and discussing the single cases one by one, the general situation is best reported in Table 3. For all the substances considered here, the agreement concerning the LO modes seems to be less satisfactory. The calculated frequencies of the phonon dispersion curves along the [001] direction

Table 3. *Vibrational spectra (cm^{-1}) at room temperature*

	Obs(1)	Obs(2)	Calc(1)	Calc(2)	Calc(3)	
A_g	242		235	209	278	
	291		268	242	313	
	322		315	286	394	
	360		365	324	408	
			431	426	449	
	452		447	447	462	
	553		530	540	513	
	573		562		543	
	629		587	619	581	
	718		668	687	700	
	798		770	786	786	
	834			803		
	921		929	819	920	
	951		948	906	1026	
	1065		1010	940	1108	
A_u		106*	209	193		
			247	223		
			296	259		
			373	313		
			455	471		
			549	548		
			596	639		
			677	671		
			981	874		
	B_{1g}	243		246	220	287
		277			256	345
		337		320	319	377
				343		
		362		373	393	427
				396		
474			455	425	435	
515			503	475	478	
550			571	573	499	
605			635	604	580	
721			684	687	617	
833			755	778	669	
891			932	800	784	
953			994	867	921	
1044			1030	931	1032	
1113			1012	1112		
B_{2g}	192	211	195	162	192	
			214			
			247			
	295		278	193	271	
	325?			234	324	
	375			308	375	
	390		400	389	382	
	410?		442	437	426	
	490?		487	489	484	
	561		566	617	561	
	649		627	638	642	
	931		976	887	948	
	B_{3g}			104	87	190
		203		196	185	212
		208		217	247	301
310			331	322	339	
325			365	377	407	
405				418	429	
420			450	517	504	
487			513	603	595	
			569			
665			655	654	634	
980†			970	870	946	
$B_{1u}(\text{TO})$		156*		154	139	
		279		321	268	

Table 3 (cont.)

	Obs(1)	Obs(2)	Calc(1)	Calc(2)	Calc(3)
	459	457	359	392	
	490?		496	409	
	585		565	609	
	612	617	589	618	
	672	660	697	658	
	936		967	860	
$B_{2u}(\text{TO})$	185		180	220	
	290		247	228	
	302	303	302	307	
	352	358	359	339	
	385		387	408	
	425		407	458	
	522	520	483	523	
	565	561	567	574	
	653	656	621	676	
	673		640	720	
	690	690	726	789	
	905		885	828	
	968	974	943	868	
	1020	1079	956	900	
$B_{3u}(\text{TO})$			192	207	
	221		257	239	
	290		258	276	
	308		321		
	368			348	
	389	390	389	390	
	445		444	442	
	480	480	489	542	
	522		539	562	
	595		625	696	
	738	738	692	729	
	775		709	755	
	888	894	896	797	
	938	951	931	875	
	990		960	929	
$B_{1u}(\text{LO})$	192		154	139	
	279		323	269	
	463		363	399	
			515	424	
	585		566	611	
	665		661	643	
	700		697	732	
$B_{2u}(\text{LO})$	1059		1026	994	
	185		181	221	
			248	228	
			302	314	
	361		362	348	
			391	421	
	471		415	490	
	525		485	535	
	575		593	579	
	660		621	694	
	705		717	765	
	775		726	799	
			887	828	
	1064		943	868	
$B_{3u}(\text{LO})$	1087		993	1027	
			196	209	
	224		258	240	
	290		272	296	
	308		321		
	371			357	
	402		393	392	
	475		486	534	
	508		519	556	
	567		558	563	

Table 3 (cont.)

Obs(1)	Obs(2)	Calc(1)	Calc(2)	Calc(3)
602		626	701	
749		693	743	
795		719	761	
960		897	875	
953		952	926	
1025		993	955	

Obs(1) single crystal data from ISW and SW; Obs(2) Fourier-transform IR data on powder by WB. Calculated values Calc(1) by us, Calc(2) by WB, using a shell model and the potentials given by Winkler, Dove & Leslie (1991); Calc(3) by ISW, using a rigid-ion model. *Data from neutron inelastic scattering in WB; for the lowest B_{1u} frequency the corresponding IR measurement is given as 192 cm^{-1} by ISW and SW. † 927 cm^{-1} in WB.

Table 4. Frequencies in the phonon dispersion curves along [001] (cm^{-1})

q		A4	A3	A1	A3	A1	A3
0,0,0.1	Obs	35	35	60	109	158	217
	Calc	30	32	59	107	158	214
0,0,0.2	Obs	64	64	115	115	169	231
	Calc	59	63	112	114	172	221
0,0,0.3	Obs	98	98	148	122	198	
	Calc	86	92	148	123	202	215
0,0,0.4	Obs	112	112	171	123		206
	Calc	108	116	169	135	239	202
0,0,0.5	Obs	125	125	143?	188		188
	Calc	120	121	150	151	260	175

Observed data from Fig. 5 in WB. Symmetry labelling from our calculations only (not assigned in the experimental measurements).

are reported in Table 4, together with the corresponding experimental and calculated values reported by WB; here the agreement is quite good.

ADP's at room temperature (298 K), calculated for all the independent atoms in the crystal structure using our empirical potentials reported in Table 2, are shown in Table 5. For comparison, in the same table the corresponding experimental data obtained from other crystal structure refinements are also reported. The first set of such data, here countersigned as obs(1) is our own; the second set [obs(2)] was obtained by WG. All these data were derived from refinement of the crystal structure of pure natural samples. The excellent agreement with the experimental results *even at different temperatures* once again prove the essential correctness and physical significance of our lattice-vibrational model, empirical potentials and of the experimental ADP's, as they are obtained from accurate crystal structure refinement and are in complete correspondence with a series of similar results we obtained for organic molecular crystals and for a number of other minerals (Gramaccioli, 1987; PDG90c; PDG93; PDG94; PDG95; PDG96a,b). Here, particularly remarkable is the U_{33} parameter for O(C), which is much higher than either U_{11} or U_{22} for the same atom and the corresponding values for all the other O atoms in the structure: such a situation is also perfectly reproduced in the calculated values.

Table 5. *Anisotropic and equivalent displacement parameters ($\times 10^4$) for andalusite*

The temperature factor is in the form:
 $T = \exp[-2\pi^2(U^{11}h^2a^2 + \dots + 2U^{23}klb \cdot c^*)]$.

		U^{11}	U^{12}	U^{13}	U^{22}	U^{23}	U^{33}	U_{eq}
Andalusite (298 K)								
Al1	Calc	68	18	0	43	0	28	46
	Obs(1)	69	17	0	51	0	37	52
Obs(2)	Calc	65	16	0	92	0	36	64
	Z.p.	28	6	0	21	0	16	22
Al2	Calc	37	-2	0	33	0	40	37
	Obs(1)	36	0	0	45	0	46	42
Obs(2)	Calc	28	0	0	82	0	44	51
	Z.p.	19	-1	0	18	0	20	19
Si	Calc	31	-1	0	31	0	30	31
	Obs(1)	34	0	0	39	0	42	38
Obs(2)	Calc	22	0	0	76	0	39	46
	Z.p.	15	0	0	15	0	15	15
O(A)	Calc	63	-10	0	35	0	38	45
	Obs(1)	63	-5	0	47	0	51	54
Obs(2)	Calc	55	-9	0	88	0	47	63
	Z.p.	33	-4	0	21	0	24	26
O(B)	Calc	39	-9	0	42	0	37	39
	Obs(1)	47	-13	0	62	0	50	53
Obs(2)	Calc	34	-18	0	98	0	48	60
	Z.p.	22	-5	0	25	0	23	23
O(C)	Calc	36	2	0	34	0	111	60
	Obs(1)	39	2	0	44	0	130	71
Obs(2)	Calc	31	6	0	85	0	135	84
	Z.p.	20	2	0	20	0	46	29
O(D)	Calc	51	-10	-6	52	8	35	46
	Obs(1)	59	-14	-10	66	13	50	58
Obs(2)	Calc	49	-12	-9	101	11	47	66
	Z.p.	28	-3	-3	28	4	21	26
Andalusite (673 K)								
Al1	Calc	146	40	0	90	0	55	97
	Obs(2)	160	47	0	145	0	63	123
Al2	Calc	76	-4	0	67	0	83	75
	Obs(2)	65	-3	0	117	0	84	89
Si	Calc	62	-2	0	63	0	61	62
	Obs(2)	62	0	0	104	0	72	79
O(A)	Calc	127	-21	0	65	0	73	88
	Obs(2)	123	-19	0	120	0	86	110
O(B)	Calc	76	-19	0	82	0	69	76
	Obs(2)	80	-28	0	142	0	89	104
O(C)	Calc	68	4	0	64	0	237	129
	Obs(2)	71	6	0	123	0	255	150
O(D)	Calc	102	-23	-14	104	17	67	90
	Obs(2)	117	-25	-24	164	24	91	124
Andalusite (873 K)								
Al1	Calc	188	52	0	115	0	71	125
	Obs(2)	213	66	0	177	0	77	156
Al2	Calc	97	-6	0	85	0	106	96
	Obs(2)	83	-6	0	142	0	102	109
Si	Calc	79	-3	0	80	0	77	79
	Obs(2)	80	3	0	123	0	89	97
O(A)	Calc	163	-28	0	83	0	93	113
	Obs(2)	148	-28	0	142	0	109	133
O(B)	Calc	97	-25	0	104	0	88	96
	Obs(2)	99	-37	0	174	0	105	126
O(C)	Calc	87	6	0	81	0	305	158
	Obs(2)	99	12	0	139	0	336	191
O(D)	Calc	130	-29	-18	132	22	85	116
	Obs(2)	151	-34	-33	199	31	113	154
Andalusite (1073 K)								
Al1	Calc	231	64	0	141	0	86	153
	Obs(2)	265	84	0	212	0	92	190

Table 5 (cont.)

		U^{11}	U^{12}	U^{13}	U^{22}	U^{23}	U^{33}	U_{eq}
Al2	Calc	119	-7	0	104	0	130	118
	Obs(2)	102	-3	0	158	0	124	128
Si	Calc	97	-4	0	98	0	95	97
	Obs(2)	102	3	0	136	0	106	115
O(A)	Calc	200	-34	0	101	0	113	138
	Obs(2)	188	-30	0	158	0	127	158
O(B)	Calc	118	-30	0	127	0	106	117
	Obs(2)	126	-47	0	215	0	120	154
O(C)	Calc	105	7	0	98	0	374	192
	Obs(2)	99	12	0	149	0	402	217
O(D)	Calc	159	-36	-22	162	27	104	142
	Obs(2)	185	-37	-37	225	40	135	182
Andalusite (1273 K)								
Al1	Calc	273	76	0	166	0	102	180
	Obs(2)	330	112	0	244	0	109	228
Al2	Calc	140	-8	0	123	0	154	139
	Obs(2)	130	3	0	187	0	141	153
Si	Calc	114	-5	0	116	0	112	114
	Obs(2)	130	0	0	155	0	125	137
O(A)	Calc	236	-40	0	119	0	133	163
	Obs(2)	225	-44	0	184	0	153	187
O(B)	Calc	139	-36	0	150	0	125	138
	Obs(2)	169	-59	0	234	0	145	183
O(C)	Calc	124	8	0	115	0	443	227
	Obs(2)	126	19	0	168	0	479	258
O(D)	Calc	188	-43	-26	191	31	122	167
	Obs(2)	222	-56	-50	256	44	160	213
Kyanite (298 K)								
Al1	Calc	31	9	6	39	5	27	32
	Obs(2)	30	18	-9	58	2	65	52
Al2	Calc	38	11	7	30	1	28	32
	Obs(2)	43	23	-9	46	-6	68	53
Al3	Calc	36	9	9	27	5	34	32
	Obs(2)	39	20	-7	43	0	76	53
Al4	Calc	37	12	7	28	5	34	32
	Obs(2)	41	20	-7	43	4	76	54
Si1	Calc	27	7	6	26	2	26	26
	Obs(2)	27	18	-7	37	0	66	44
Si2	Calc	27	8	5	25	2	25	26
	Obs(2)	25	18	-13	40	-2	60	43
O(A)	Calc	36	6	4	28	3	42	37
	Obs(2)	50	18	-13	49	-4	91	66
O(B)	Calc	33	10	7	31	4	32	32
	Obs(2)	41	15	-11	52	2	66	56
O(C)	Calc	44	10	4	31	5	31	36
	Obs(2)	55	21	-9	58	2	77	65
O(D)	Calc	44	15	14	35	9	35	36
	Obs(2)	59	26	2	49	10	82	63
O(F)	Calc	33	8	5	32	3	30	32
	Obs(2)	43	18	-17	55	-10	72	60
O(G)	Calc	42	10	13	35	-3	34	36
	Obs(2)	62	23	-4	55	-4	82	67
O(H)	Calc	41	14	4	38	-3	31	37
	Obs(2)	59	33	-6	66	-4	71	65
O(K)	Calc	32	14	5	43	2	32	35
	Obs(2)	52	33	-9	63	2	77	64
O(E)	Calc	35	14	11	33	6	43	36
	Obs(2)	57	28	0	55	12	77	62
O(M)	Calc	32	4	8	37	1	33	35
	Obs(2)	46	15	-7	58	-4	83	65

Obs(1): our data at 295 K; Obs(2): WG; Calc: our calculated values. The labelling of the atoms is the same as in WG. For all the experimental data shown in this table, the reported standard deviations are of the order of the last digit, or even considerably lower. In particular, the e.s.d.'s for our data in each case are below 0.0002 \AA^2 .

Table 6. Bond distances (\AA) at different temperatures, uncorrected (from WG) and corrected for thermal motion

Standard deviations are ca 0.002–0.004 \AA

T (K)	298		673		873		1073		1273	
	Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected	Corrected
Al1—O(A)	1.827	1.831	1.828	1.836	1.828	1.838	1.829	1.841	1.831	1.846
Al1—O(B)	1.891	1.895	1.892	1.899	1.892	1.901	1.893	1.904	1.893	1.906
Al1—O(D)	2.086	2.089	2.112	2.117	2.126	2.132	2.138	2.145	2.154	2.163
Average	1.935	1.938	1.944	1.951	1.949	1.957	1.953	1.963	1.959	1.972
Al2—O(A)	1.816	1.820	1.818	1.825	1.821	1.830	1.823	1.833	1.823	1.836
Al2—O(C)	1.839	1.844	1.845	1.854	1.846	1.856	1.851	1.866	1.853	1.870
Al2—O(C)	1.899	1.903	1.907	1.915	1.909	1.919	1.913	1.925	1.922	1.936
Al2—O(D)	1.814	1.818	1.816	1.823	1.816	1.825	1.817	1.828	1.818	1.831
Average	1.836	1.841	1.840	1.847	1.842	1.851	1.844	1.856	1.847	1.861
Si—O(B)	1.645	1.648	1.646	1.651	1.647	1.653	1.646	1.654	1.650	1.659
Si—O(C)	1.618	1.622	1.616	1.624	1.619	1.629	1.619	1.631	1.618	1.632
Si—O(D)	1.630	1.633	1.629	1.635	1.630	1.638	1.629	1.638	1.628	1.639
Average	1.631	1.634	1.630	1.636	1.632	1.640	1.631	1.640	1.631	1.642

A slight systematic overall disagreement can be noticed, since in general the calculated values are smaller than our corresponding observed data. However, the theoretical estimates of ADP's and those of thermodynamic functions are strongly connected [see equations (1)–(4)] and on these grounds if the calculated ADP's were underestimated, then the calculated values of thermodynamic functions would also be underestimated, just contrarily to what actually happens. For this reason, more than to inadequacies of our lattice-dynamical model, the slight systematic overall disagreement might be due instead to a number of circumstances and, in particular, to an unsatisfactory accounting of the absorption, extinction or background effects.

Some systematic disagreement can also be noticed, particularly in the U_{22} parameters observed by WG; here for all the atoms and at all temperatures the observed values are consistently higher than the corresponding calculated estimates by an almost constant value (0.0060 \AA^2). In our opinion such a situation derives from experimental errors and very probably to inadequate correction for absorption or extinction. In WG's work the data were obtained from a spherically ground crystal 250 m in diameter and no correction for these effects was performed; a possibility is that the diameter of the sample was not constant. The presence of systematic experimental errors in WG's data is confirmed by our own experimental results, where all the U_{22} 's are much closer to the corresponding calculated values and are quite different from those of WG.

In Table 5 the zero-point (z.p.) contribution, evaluated according to our calculations, is also reported for each component of the U tensors. As with all the silicates and oxides we have examined so far, this contribution (about one half of the room-temperature value) is remarkably large and far from being negligible. Unfortunately, for minerals too few reliable measurements at very low temperature are available to be able to verify our theoretical predictions; in any case, our estimates for minerals

Table 7. Values of thermodynamic functions ($J \text{ mol}^{-1} \text{ K}^{-1}$)

T (K)	S_{obs}	S_{calc}	C_{pobs}	C_{pcalc}
Andalusite				
100	12.53	11.10	29.70	31.86
120	18.95	17.96	41.11	43.71
140	26.14	25.58	52.47	55.52
180	41.94	42.27	73.86	77.73
200	50.25	50.99	83.79	87.83
240	67.11	68.64	101.3	105.8
280	83.89	86.11	116.4	120.9
298	91.39	93.83	122.6	126.6
320	100.3	103.1	128.9	133.4
350	112.2	115.4	136.9	141.3
380	123.7	127.3	144.0	148.3
			146.6*	
400		135.0	150.7	152.4
450			159.4	
485			164.4	
Kyanite				
100	8.26	6.49	23.17	23.83
120	13.48	11.83	34.52	35.24
140	19.69	18.16	46.41	47.17
180	34.17	32.86	69.51	70.41
200	42.04	40.83	80.16	81.13
240	58.38	57.37	99.09	100.2
280	74.88	74.07	115.0	116.3
298	82.30	82.80	121.6	122.7
320	91.12	90.50	128.1	129.6
350	103.0	102.5	136.6	138.0
380	114.5	114.2	143.7	145.3

The $C_p - C_v$ differences and the corrections to the calculated value of entropy (PDG96b) have been obtained using the data concerning thermal expansion and compressibility reported by WB for andalusite, and by WG and Brace, Scholtz & La Mori (1969) for kyanite. The crystal data used in our calculations correspond to our own at room temperature. For andalusite and kyanite, the observed thermodynamic data up to 380 K are taken from Robie & Hemingway (1984); above this temperature, from Salje (1986). *From Salje (1986) at 380 K.

confirm the experimental results obtained by Smith, Artioli & Kvik (1986) and also, more recently, by Pavese, Artioli & Prencipe (1995).

Another interesting observation can be drawn concerning the possibility of correcting the bond distances for thermal motion. According to Johnson (1970, 1980)

Table 8. *Vibrational spectra of kyanite (cm⁻¹)*

Ag	Obs							302		325	
	Calc	200	211	237	259	270	285	297	313	315	324
	Obs			360				405	419		437
	Calc	334	342	366	380	384	392	414	416	425	445
	Obs				486						562
	Calc	467	481	482	487	498	530	542	561	569	577
	Obs					669					
	Calc	583	607	634	650	667	673	689	705	712	726
	Obs				952						
	Calc	903	913	944	955	965	970	981	1003		

Observed Raman data from Mernagh & Liu (1991).

and Scheringer (1972) we have

$$r_c = r_o + [tr(\mathbf{Z}) - \mathbf{r}'_o \mathbf{Z} \mathbf{r}_o / r_o^2] / 2r_o, \quad (13)$$

where r_c and r_o are the corrected and the uncorrected distances between the atoms i and k , respectively, \mathbf{r}_o is the vector corresponding to the atomic distance and \mathbf{Z} is a matrix defined as

$$\mathbf{Z} = \mathbf{U}_i + \mathbf{U}_k - \mathbf{U}_{ik} - \mathbf{U}_{ki}, \quad (14)$$

in which besides the ADP tensors $\mathbf{U}_i = \langle \mathbf{u}_i \mathbf{u}_i' \rangle$ and $\mathbf{U}_k = \langle \mathbf{u}_k \mathbf{u}_k' \rangle$, we also have the correlation tensors \mathbf{U}_{ik} 's = $\langle \mathbf{u}_i \mathbf{u}_k' \rangle$, which cannot be obtained from Bragg diffraction measurements. However, all these tensors can be evaluated from lattice dynamics together with the usual \mathbf{U} 's [see, for instance, Willis & Pryor (1975), equation 4.86*b*, where polarization vectors for different atoms should replace those for the same atom] and if our calculations provide acceptable agreement with the experimental \mathbf{U} 's, in view of the close similarity in the calculating procedure and routines, there is also good reason to believe the estimates of the correlation tensors \mathbf{U}_{ik} to be correct.

On applying these considerations and procedures to the bond distances, starting from the crystal structure data at the temperatures reported by WG, and using our lattice-dynamical estimates for \mathbf{U}_{ik} 's and \mathbf{U} 's, we obtained the corrected distances for andalusite at various temperatures, as reported in Table 6. As with other silicates we have examined (PDG90*c*; PDG95), and with quartz (PDG94), the correction amounts to a few thousandths of an Å (0.003–0.004 Å at room temperature up to ~ 0.015 Å at 1273 K). Here, especially for the Si—O bonds, the situation is similar to that which we already observed for diopside (PDG96*b*): the uncorrected values remain almost constant, at least up to *ca* 1000 K, whereas the corrected values increase on increasing temperature. This phenomenon can be ascribed to an essential rocking motion of the almost rigid SiO₄ tetrahedron, which tends to lower the values of the uncorrected distances, similar to that which usually happens in rigid molecules: here, this apparent shrinkage almost equals the increase in the real values of the Si—O bond lengths, which takes place on increasing the temperature.

Such a situation is somewhat different from our results for fayalite (PDG95), where the corrected values of the Si—O bonds seem to remain virtually temperature-independent. However, in the olivine group the SiO₄ tetrahedra are hard isolated units surrounded by relatively soft Mg—O bonds, which are those more affected by thermal expansion; whereas in diopside the tetrahedra are linked together and in andalusite the Al—O bonds are stronger than the Mg—O bonds: for this reason, for diopside and andalusite, thermal expansion is more likely to affect the whole structure. Furthermore, some attention should also be given to the lower accuracy of the ADP's (and also of crystallographic data in general) concerning the structure of the minerals of the olivine group at different temperatures (see PBG90*c*, PDG95 for a more detailed discussion).

Calculated values of thermodynamic functions, such as the specific heat C_p and entropy S , at different temperatures according to our model and procedure are reported in Table 7: here they are compared with the corresponding experimental values obtained by Robie & Hemingway (1984) or Salje (1986). Since there are no data for either the volume expansion coefficient α or for the bulk modulus K_T at low temperature, no calculations have been performed below 100 K and above such a temperature both α and K_T were considered to be constant. The agreement for either C_p and S is fairly good: for instance, at room temperature (298 K) the difference between these calculated values and the corresponding experimental data is 3.3 and 2.7%, respectively, and the situation remains satisfactory over the whole range of temperatures. This is another proof of the reliability of lattice-dynamical calculations and of our procedure in particular. The excellent results found for a group of silicates by other authors, such as Winkler, Dove & Leslie (1991) and Patel, Price & Mendelsohn (1991), by lattice dynamics, concerning transferability of empirical potentials within a wide group of substances, are also confirmed.

5. Sillimanite and kyanite

Besides andalusite, there are two more phases of the compound Al₂OSiO₄ widely occurring in nature as minerals: sillimanite and kyanite. Since it is not uncommon for all three minerals to occur together in the same rock, such an occurrence is a classic natural example of a triple point and a notable number of mineralogical and petrological papers have been dedicated to the subject [see, for instance, Salje (1986) for details and a list of useful references]. Differently from andalusite, where the two independent Al atoms in the crystal structure are, respectively, six- and fivefold coordinated, in sillimanite there are also two independent Al atoms, having, however, six- and fourfold coordination, respectively, whereas in kyanite there are four independent Al atoms,

all of them with a sixfold almost octahedral coordination. Since the crystal structures of these phases have also been determined (see, for instance: WG; Peterson & McMullan, 1986) and for kyanite even at different temperatures (WG), in view of the possible extensive application of our potentials and of lattice dynamics in general, we tried to apply our routines and potentials to both sillimanite and kyanite.

For sillimanite some of the calculated frequencies are imaginary and, therefore, our potentials are not acceptable. A plausible explanation concerns the presence of the four-coordinated Al atom, whose set of bonds (with oxygen) is notably different from the usual set (bond lengths and angles) of Al—O bonds occurring in all the other minerals we have considered so far in our calculations and to which our potentials have been fitted.

For kyanite, where all the Al atoms instead show a sixfold coordination, the calculated frequencies are very reasonable throughout the whole Brillouin zone: however, the symmetry is triclinic ($P\bar{1}$) and there are only two possibilities for the symmetry of the Raman- or IR-active vibrational modes (*i.e.* A_g and A_u , respectively) at the origin. As a consequence, and also because a considerable number of independent atoms in the unit cell ($Z=8$) are present, an almost continuous series of frequencies in the 100–1000 cm^{-1} interval for both the A_g - and the A_u -modes is expected, so that no useful comparison with the experimental data can be carried out. Such a situation is evident on looking at Table 8, where the calculated frequencies are compared with the (very few) peaks in the Raman spectrum observed by Mernagh & Liu (1991), which are the only experimental data of this kind available in the literature for kyanite.

Calculated estimates of entropy S and of the specific heat C_p are shown in Table 7; at room temperature; the disagreement with the corresponding experimental values is 0.6% for S and 0.9% for C_p , and these remain almost the same for a wide range of temperatures. At 100 K, or just above this temperature, the discrepancy between the observed data and our theoretical estimates is greater; however, such a situation is not surprising on considering our assumption of the constant expansion coefficient α , which does not hold especially at low temperature (see above). In any case, it is interesting to notice that our vibrational model clearly accounts for the notable entropy difference between andalusite and kyanite.

With respect to the ADP's, no agreement with the experimental values has been achieved: an example is given in Table 5 where the data obtained by WG from crystal structure refinement at room temperature are reported together with the results of our calculations. The difference is quite striking, especially if compared with the case of andalusite. However, almost all the observed data are about twice as great as the corresponding calculated estimates (see, for instance, the equivalent B 's) and, if our calculations were inadequate, then our

estimates of thermodynamic functions would also be largely in error (see above: here they should be by far too small), owing to the strong theoretical link between these quantities; instead, our estimates for thermodynamic functions at various temperatures are excellent (see Table 7).

Since, as we have seen, the experimental values of the U 's for kyanite are inconsistent with thermodynamic data, and the crystallographic results are likely to be seriously affected by errors (see above), our calculated U 's in Table 5 for this mineral are reported mainly as theoretical predictions, in want of adequate experimental confirmation.

6. Conclusions

Our application of harmonic lattice dynamics to andalusite and (at least in part) to kyanite confirms the possibility of deriving ADP's, vibrational frequencies and thermodynamic functions using a routine procedure and transferable empirical potentials. In particular, for all these applications here the rigid-ion model seems to afford results whose quality is comparable to that provided by more complex models, such as the shell model.

With respect to other statistical-mechanical procedures, such as that proposed by Kieffer (1979*a,b*; 1980), which has been extensively applied to minerals, the Born-von Karman lattice-dynamical model is not only more accurate, but no fit to a number of experimental specific data for a single phase is needed; for these reasons our opinion is shared by other authors, such as, for instance, WB. For all these uses, transferability of potentials (at least within certain groups of substances) is very important: if such a property is further confirmed, and better sets are obtained, the possibility of deriving thermodynamic properties of a certain mineral starting from crystal structure data only might appear as definite. Such a derivation might take place even *a priori* if procedures of modelling crystal structures are adequately developed, thereby envisaging the possibility of predicting the existence of all the possible phases of a certain substance and their field of stability. Here a fundamental point is establishing *what level of accuracy* can be indeed attained: contrary to what appears to be a widespread belief, the problem *does not only involve the limitations of the theoretical model and computational routines*, since in the vibrational spectral data currently available there still are a consistent number of errors in establishing and measuring the fundamental frequencies, especially the lowest ones, and unfortunately there is also a fundamental lack of measurements of phonon dispersion curves. For all these reasons, there is no question about the possibility of a notable improvement of the calculated results and potentials, even if the same method and routines we have used so far are continued to be used in the present stage.

Another interesting aspect of our results is the good to excellent agreement between thermal parameters obtained from accurate crystal structure refinement and their theoretical counterparts. As with the similar conclusions we have reached for organic molecular crystals (Gramaccioli, 1987, 1992; Filippini & Gramaccioli, 1989, and references therein) and for other minerals (see the *Introduction*), besides confirming the physical significance of such crystallographic data, if obtained from accurately refined structures, this agreement supports the validity of a parallel evaluation of correlation tensors between the displacement of different atoms, thereby permitting bond length correction for thermal libration in a general case, which until quite recently has only been mentioned as a theoretical possibility.

Whenever the agreement with the experimental data is not quite satisfactory, then a reasonable explanation can always be found: in any case so far observed, the explanation does not affect the general validity of the theoretical routine followed here. For instance, the impossibility of having reasonable results for sillimanite is almost certainly connected with the presence of fourfold-coordinated aluminium; similarly, for andalusite, the somewhat inferior quality of the estimates of thermodynamic functions might be due to the need for an adequate reconciling of the requirements of the potentials involving five- or six-fold coordinated aluminium. The disagreement concerning the U_{22} 's in andalusite is most probably due to absorption and the general disagreement for kyanite is almost certainly due to the insufficient good quality of the crystals, especially if the ADP's and not only the atomic coordinates of good quality are needed. For kyanite and andalusite the disagreement in thermodynamic properties at low temperature is explained by the lack of measurements of the thermal expansion coefficient α (and of the bulk modulus): under these conditions, especially for α , the values are notably different from those at room temperature. A similar situation has occurred in our former works on the subject (see, for instance, PDG94, PDG95, PDG96*a,b*): although sometimes the dependence on temperature of at least the expansion coefficient α was known, a correction according to expression (12) was never applied.

As a last remark, since the displacements at 0 K are far from negligible, in general the physical significance of models with stationary atoms at 0 K should be considered with caution, whilst having a clear and precise idea about the applications for which they are intended to be used.

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