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Atomic Thermal Parameters and Thermodynamic Functions for Corundum (α -Al₂O₃) and Bromellite (BeO): a Lattice-Dynamical Estimate

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Abstract

A harmonic valence-force-field rigid-ion lattice-dynamical model fitted to Raman and IR spectral data and extended throughout the whole Brillouin zone has been used to calculate the atomic displacement parameters, entropy and molar heat capacity for corundum (α -Al₂O₃) and bromellite (BeO). The agreement with experimental data is good.

Introduction

In the last few years, the importance and physical significance of crystallographic atomic thermal parameters (or atomic displacement parameters, a.d.p.s) have been emphasized by chemists and physicists [see, for example, Pilati, Bianchi & Gramaccioli (1990*b*) and references therein]; at the same time, considerable interest in this subject has also been developed by mineralogists [see, for example, Downs, Gibbs & Boisen (1990) and references therein].

It is well known (Willis & Pryor, 1975) that theoretical estimates of a.d.p.s can be best obtained from lattice dynamics, following the procedure first described by Born & von Karman (1912, 1913) using a conveniently sampled set of values of the wave vector \mathbf{q} in the Brillouin zone [corresponding to the

reciprocal unit cell of the crystal; a recent discussion of such sampling is given by Pilati, Bianchi & Gramaccioli (1990*c*)]. For a particular value of \mathbf{q} and for a harmonic model, the average energy $E_{\psi\mathbf{q}}$ of each normal mode ($\psi\mathbf{q}$) of frequency ν is

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

where h and k are the Planck and Boltzmann constants, respectively, and T is the absolute temperature. The limit as $\nu \rightarrow 0$ of the above expression is

$$\lim_{\nu \rightarrow 0} E_{\psi\mathbf{q}} = \lim_{\nu \rightarrow 0} [kT/\exp(h\nu/kT)], \quad (2)$$

which shows that the contribution to vibrational energy grows when the frequency is decreased. This happens because the lowest vibrational-energy levels are more populated than the highest levels, a phenomenon that is enhanced for low temperatures.

From these data and the mass-adjusted polarization vectors $\mathbf{e}_{p,\psi\mathbf{q}}$ of the atom p in the unit cell, which are part of the eigenvectors of the dynamical matrices $\mathbf{D}(\mathbf{q})$, the a.d.p.s \mathbf{U}_p can be obtained as

$$\mathbf{U}_p = (Nm_p)^{-1} \sum_{\psi\mathbf{q}} E_{\psi\mathbf{q}} (2\pi\nu_{\psi\mathbf{q}})^{-2} \mathbf{e}_{p,\psi\mathbf{q}} \cdot \mathbf{e}_{p,\psi\mathbf{q}}^{*T}, \quad (3)$$

where N is the total number of unit cells in the crystal. The simulations are extended to all the vibrational

modes (ψ) for a certain value of the wave vector \mathbf{q} and to all the sampled points in the Brillouin zone, each of which corresponds to a particular value of \mathbf{q} (in principle, every possible value of \mathbf{q} in the Brillouin zone should be considered). The elements of the dynamical matrices are given by sums of the second derivatives (with respect to the mass-weighted coordinates) of the interaction energy between the atoms in the crystal multiplied by a phase factor $\exp(2\pi i \mathbf{q} \cdot \Delta \mathbf{x})$ [Willis & Pryor (1975), equation 3.10(b)]. In turn, this interaction energy is given by a Coulombic contribution and by a valence-bond deformation (plus, sometimes, a van der Waals interaction between non-bonded atoms).

Besides the a.d.p.s, the same lattice-dynamical procedure permits evaluation of very important data, such as thermodynamic functions as a function of temperature. For instance, the molar heat capacity c_v and the entropy S are given by

$$c_v = 3R \sum_{\nu} g_{\nu} \Delta \nu (h\nu/kT)^2 \times \exp(h\nu/kT) / [\exp(h\nu/kT) - 1]^2 \quad (4)$$

$$S = E_{\text{vib}}/T - 3R \sum_{\nu} g_{\nu} \Delta \nu \ln [1 - \exp(-h\nu/kT)]. \quad (5)$$

Here, E_{vib} is the (temperature-dependent) vibrational energy of the crystal and g_{ν} is a normalized density-of-states function ($\sum_{\nu} g_{\nu} \Delta \nu = 1$); the summation \sum could be carried out as in (3) for every value of ψ and \mathbf{q} but, owing to the absence of anisotropic effects in the results, it can also be carried out directly on the density-of-states function (see also Pilati *et al.*, 1990b).

The procedure of using the density of states becomes quite advantageous if the calculations are performed for different temperatures, since the lengthy process of building and diagonalizing the dynamical matrices can be performed only once. For anisotropic a.d.p.s, which cannot be obtained from the density of states g_{ν} alone, the eigenvectors of the dynamical matrices also need to be stored.

If these simplifications are adopted, the vibrational frequencies must be considered to be independent of temperature. Instead, if different sets of dynamical matrices are diagonalized (one set corresponding to the observed crystal structure at a particular temperature T and pressure P), the calculated frequencies can be rendered temperature (and pressure) dependent provided force fields depending on atomic distances are used in connection with the variation of the structural parameters.

Recently, successful models essentially based on Debye's theory with additional optic-mode contributions, determined on the basis of IR and Raman spectra (Kieffer, 1979, 1980, 1982, 1985), have been proposed to evaluate temperature-dependent ther-

modynamic functions for a variety of minerals (mostly silicates and oxides, including corundum). However, there are several good reasons to use the Born-von Karman procedure whenever possible:

(1) It is more advanced and considerably less simplified in principle. Therefore, at least in general, we should expect an improved agreement with the experimental data. This agreement is confirmed by extensive and successful use of the Born-von Karman lattice-dynamical procedures in solid-state physics.

(2) The same force fields from which the second derivatives of energy are obtained for use in the dynamical matrices could also be employed for theoretical modelling of crystal structures (on a minimum-energy basis) or for evaluation of elastic properties: on this basis, there is a possibility of the use of a unique consistent field for all purposes. There is even the possibility of combining the vibrational contribution to entropy with the estimates of potential energy and vibrational energy, so that a theoretical crystal structure corresponding to a free-energy minimum can be derived (see, for example, Filippini & Gramaccioli, 1981).

The connection with minimization of potential energy is particularly important: too often, in fact, only first derivatives are considered in minimization procedures and for this reason inconsistent results may be obtained. For instance, by examining second derivatives we have shown (Gramaccioli & Pilati, 1992) that some of the best models reported for forsterite ($\alpha\text{-Mg}_2\text{SiO}_4$) in the literature do not correspond to true energy minima, in spite of having zero first derivatives of energy with respect to both atomic coordinates and unit-cell parameters. Since the best routines available for energy minimization (e.g. *WMIN*: Busing, 1981) permit a choice between the steepest-descent method and other methods, such as the Rosenbrock or Newton-Raphson methods, which are not limited to first derivatives only, caution should be taken in selecting the best procedure.

(3) In applying Debye's model, it is necessary in each case to operate *a posteriori*, by fitting the theoretical function to the experimental values of the molar heat capacity. This is necessary to obtain the so-called Debye temperature θ of a particular substance, which is linked to the assumed maximum vibrational frequency $\nu(D)$ in the crystal: $\theta = \nu(D)/k$, where k is the Boltzmann constant. Apparently (particularly in view of the gross approximation involved), it is not possible to predict this temperature exactly for a particular crystal.

(4) In Kieffer's model, no provision is made for Raman- or IR-inactive modes or for active modes not corresponding to a measurable intensity. There is no reason, in fact, why the contribution of these modes (and of the corresponding branches in the Brillouin zone) should be negligible with respect to the others. For corundum, for instance, the A_{1u} and the A_{2g}

modes are both Raman and IR inactive; this is also true for the B_2 modes in bromellite.

(5) If the force-field constants prove to be transferable, at least within groups of similar minerals, then the derivation of the a.d.p.s and of the values of thermodynamic functions could proceed *a priori*, starting from crystal-structure data only. In principle, even these data would not be necessary if the force-field model is good enough to reproduce the structure. In short, if such procedures are successful for a sufficient number of cases, and with evaluation of the free energy possible, this could be a way of deducing the existence and the stability field of a certain phase.

For all these reasons, from our previous experience on molecular crystals (Gramaccioli, 1987) and on forsterite (Pilati *et al.*, 1990b), we have examined corundum and bromellite as particularly interesting subjects for investigation. These substances have the simplest structures involving octahedrally coordinated aluminium or beryllium bonded to oxygen and, if satisfactory empirical force fields are derived, which are able to be transferred, there is the possibility of extending these routines and force fields to a considerable number of other compounds, in particular, silicates or more complex oxides.

Since the experimental measurements of vibration frequencies presently available are nearly exclusively Raman and/or IR data, the possibility of deriving a lattice-dynamical model and an empirical force field valid in the whole Brillouin zone by fitting the observed Raman- and IR-active frequencies only would be particularly important. For forsterite, in fact, we have found (Pilati *et al.*, 1990b) that Iisshi's (1978a) field derived from the best fit with the Raman and IR spectra is also valid for interpretation of the phonon-dispersion curves, measured by Ghose, Hastings, Corliss, Rao, Chaplot & Choudhury (1987), which validates the proposed model.

A further advantage of the use of corundum and bromellite is that thermodynamic data of good quality are available in the literature (Furukawa, Douglas, McCookey & Ginnings, 1956; Chase, Curnutt, Hu, Prophet, Syverrud & Walker, 1974; Robie, Hemingway & Fisher, 1978), together with a number of papers concerning measurements and interpretation of Raman and IR spectra (Porto & Krishnan, 1967; Loh, 1968; Arguello, Rousseau & Porto, 1969; Gervais & Piriou, 1974; Gervais, Billard & Piriou, 1975; Iishi, 1978b; Kouroklis, Sood, Hochhiemer & Jayaraman, 1985) and of accurate measurements of atomic thermal parameters (Pryor & Sabine, 1964; Sabine & Hogg, 1969; Downs, Ross & Gibbs, 1985; Hazen & Finger, 1986). Even for corundum, there are particularly accurate measurements of the a.d.p.s (Spackman, Stewart & Le Page, 1981; Lewis, Schwarzenbach & Flack, 1982; Kirfel & Eichhorn, 1990). For bromellite, phonon-dispersion curves are also available (Brugger, Strong & Carpenter, 1967; Ostheller,

Schmunk, Brugger & Kearney, 1968), together with their interpretation in terms of a valence-force-field (VFF) rigid-ion model (Ramani, Mani & Singh, 1976).

The reason why a Born-von Karman lattice-dynamical model has not been frequently used lies, at least in our opinion, in the difficulties of such calculations, especially if sophisticated versions like the so-called shell model or other models involving ion polarizability are used. Here our calculations are limited to the comparatively simple rigid-ion model, where the atomic charges are assumed not to vary during motion and the centres of charge distribution are assumed to coincide with the atomic centres at any instant.

This assumption can be subject to criticism, since the rigid-ion model is well known to be inadequate for a satisfactory lattice-dynamical treatment of substances where the atomic charges are not small. This inadequacy is especially evident in evaluating some properties such as the dielectric constant (Cochran, 1973). The discrepancy between the results from a rigid-ion model and the experimental data appears to be large for the highest frequencies, whereas there is good agreement for lower frequencies. A classic example for this is given by the phonon-dispersion curves of alkali halides (see, for example, Woods, Cochran & Brockhouse, 1960; Cochran, 1973). Another good example is given by the curves for forsterite, where the lower branches of the measured curves were satisfactorily interpreted by Rao, Chaplot, Choudhury, Ghose, Hastings & Corliss (1988) using a rigid-ion model; even a rigid-group model for the SiO_4 tetrahedron was sufficient for these purposes.

Because of the good agreement with the lower frequencies, the rigid-ion model might be quite useful, in spite of its limitations. For instance, as we have seen for the a.d.p.s [see (2) and (3) above], at least if the temperature is not too high, the highest vibrational levels are substantially empty and, for this reason (for pure compounds and apart from spin-ordering effects, absent here), the values of thermodynamic functions are essentially determined by the lowest vibrational levels.

The above explains the satisfactory agreement we have obtained using a rigid-ion model in calculating the a.d.p.s and thermodynamic functions for forsterite (Pilati *et al.*, 1990b), and justifies the use of similar models in further works of this kind.

In spite of the greater success of the shell model, which has also been used to reproduce the experimental values of thermodynamic functions for forsterite (Price, Parker & Leslie, 1987), for this model and its more advanced versions where non-Coulombic interactions extend beyond the next neighbours, besides the obvious complexity of the calculations, a serious inconvenience is given by 'the

large number of free parameters and the unreal values some of them sometimes assume when they are determined by least-squares analysis of experimental dispersion curves' (Ghose, 1985). Needless to say, we agree with this statement; on the other hand, we do not claim to perform a complete lattice-dynamical analysis and for this reason our attention (and conclusions) will be essentially limited to the values of a.d.p.s and of thermodynamic functions.

Calculation procedure

For our calculations, the same routines used by us for forsterite (Pilati, Bianchi & Gramaccioli, 1990*a, b, c*) were adopted. The only addition to our set of computer programs was the possibility of improvement of the force field through a best-fit basis to the observed Raman- and IR-active frequencies ν by minimization of the function $\sum_i w_i (\nu_{i(\text{obs})} - \nu_{i(\text{calc})})^2$, where the weights w_i are given by $1/\nu_{i(\text{obs})}^2$. This weighting scheme was chosen to emphasize the importance of the lower frequencies, as mentioned above. For the process of minimization itself, the program VA04A (QCPE program no. 60) based on a generalization of the least-squares method (Powell, 1965) was adopted.

Another addition concerns a delicate problem, which had never appeared in our former calculations on molecular crystals even for forsterite: this problem arises when three-body interactions (as, for instance, bond-angle bending) extend throughout an indefinite chain. For a molecule (or for an isolated 'molecular' group like the SiO_4 tetrahedron), the situation is much simpler, since all the bond angles (corresponding to non-zero force constants) can be codified to take place within the same set of atoms, whereas in the general case attention should be given to the difference between atoms related to each other by unit-cell translations: these atoms should not be considered as equivalent for a non-integral value of the wave vector \mathbf{q} .

In calculating the second derivatives, the complication of three-body interactions has been solved by introducing additional atoms l , each related to the atom p' by the unit-cell translation $\Delta\mathbf{r}(p', l)$. The derivatives with respect to the VFF coordinates are then referred to the coordinates of the corresponding atoms p and p' in the unit cell: during this operation, the results are multiplied by the phase factor $\exp[2\pi i \mathbf{q} \cdot \Delta\mathbf{r}(p', l)]$. Thus, the expression becomes

$$\Phi^{pp'} = \mathbf{S}_l \mathbf{K} \mathbf{S}^T \exp[2\pi i \mathbf{q} \cdot \Delta\mathbf{r}(p', l)], \quad (6)$$

where the components of $\Phi^{pp'}$ (the force-constant matrix involving the atoms p and p') are given by

$$\Phi_{ij}^{pp'} = \partial^2 E / \partial x_i^p \partial x_j^{p'}. \quad (7)$$

\mathbf{K} is a force-constant matrix with respect to VFF variables (e.g. bond-angle bending, bond stretching)

Table 1. *Parameters of the force fields used*

Stretching force constants ($10^{-8} \text{ N } \text{\AA}^{-1}$; d in \AA)	
Al-O	1.404-1.581 (d : 1.914)
Be-O	1.897
Bending force constants ($10^{-8} \text{ N } \text{\AA} \text{ rad}^{-2}$)	
O-Al-O	0.54318
O-Be-O	0.21555
Stretching-stretching force constants ($10^{-8} \text{ N } \text{\AA}^{-1}$)	
Al-O bonds joined to the same Al atom	-0.01675
Be-O bonds joined to the same Be atom	0.06812
Stretching-bending force constants ($10^{-8} \text{ N } \text{ rad}^{-1}$)	
Al-O bonds and O-Al-O angles centred on the same Al atom	0.16615
Be-O bonds and O-Be-O angles centred on the same Be atom	0.08536
Bending-bending force constants ($10^{-8} \text{ N } \text{\AA} \text{ rad}^{-2}$)	
O-Al-O angles sharing a side	-0.02577
O-Al-O angles sharing the Al atom only	-0.06766
Atomic charge (in electron units)	
Z(Al)	-1.455
Z(Be)	-0.97
Z(O)	0.97

and the components of \mathbf{S} and \mathbf{S}_l are the first derivatives of these VFF variables with respect to the atomic coordinates of the atoms p and l .

This method becomes particularly useful and easy to use (with no additional coding necessary) in the most general case and also allows for the possibility of using any kind of interaction constants (e.g. bending-stretching, stretching-stretching). For corundum and bromellite, this procedure becomes essential, owing to the presence of a network of bond angles extending along the three dimensions throughout the crystal and to the particular importance of bond-angle bending and of interaction constants in these compounds (see below).

Results and discussion

In Iishi's (1978*b*) work, the IR and Raman spectra of corundum were interpreted on the basis of various Urey-Bradley models, each of them in turn applied to short-range (SR), rigid-ion (RI) and two variants of polarizable-ion (PI1 and PI2) lattice-dynamical models. Apparently, none of these models have been extended beyond the origin of the Brillouin zone. Owing to the octahedral bond set around the Al atom, it was not clear how to use Iishi's Urey-Bradley force fields in our program in perfect agreement with the author. For this reason, it was easier for us to derive a new VFF using the minimization routine described above: the data on this field are given in Table 1. Differently from other cases, where the interaction constants are of relatively minor importance, here their use, especially for bending-stretching constants, is essential to obtain a reasonable fit to the observed values. This is probably due to the relatively low value of the Al-O stretching-force constants and to the

Table 2. *Vibration frequencies at $q = 0$ (cm^{-1})*

Column 1 shows the experimental measurements: for corundum, Raman data are from Porto & Krishnan (1967); IR data from Gervais & Piriou (1974) and Gervais *et al.* (1975); for bromellite, the experimental data are from Loh (1968) and Arguello *et al.* (1969). Column 2 shows our calculated data. Column 3 reports the corresponding values of Iishi (1978*b*) (corundum, rigid-ion model) and Ramani *et al.* (1976) (bromellite, A3 model). The *R* index at the end of the calculated values shows the agreement with the experimental data. The experimental data are from Gieske & Barsch (1968) and from Cline *et al.* (1967) for corundum and bromellite, respectively.

	Obs.	Calc. (1)	Calc. (2)
Corundum			
A_{1g}	418	422	455.2
	645	645	659.2
E_g	378	396	380.3
	432	431	442.1
	451	472	472.3
	578	560	531.0
	751	689	733.2
A_{2u} TO	400	417	395.5
	584	580	574.2
E_u TO	385	387	394.0
	439	454	454.2
	570	590	595.8
	635	653	665.7
A_{2u} LO	514	419	401.3
	887	849	860.6
E_u LO	388	391	383.9
	482	486	426.0
	631	654	652.3
	908	838	846.9
A_{1u}		493	
		623	
A_{2g}		379	
		528	
		711	
<i>R</i>		0.041	0.050
Bromellite			
E_1 TO	725	736	713
E_2	340	343	440
	680	685	696
A_1 TO	684	700	692
E_1 LO	1095	1067	1095
A_1 LO	1085	1042	1082
B_2		580	
		881	
<i>R</i>		0.025	0.032

relatively high value of the O–Al–O bond-bending constants, accounting for the presence of a considerable number of vibrational modes involving simultaneous bond bending and stretching. It has also been useful to assume a linear dependence of the Al–O stretching constant upon bond distance: here (see Table 1), the coefficient is negative, in agreement with the tendency of the longest bonds to become weaker, and the average Al–O bond distance in this structure is 1.914 Å.

The good agreement of our calculations with the measured frequencies is evident in Table 2, where the experimental measurements of Raman- and IR-active frequencies are reported (first column), together with the results of our calculations (second column), and the corresponding results obtained by Iishi's rigid-ion model. As for crystallographic calculations, the agree-

ment is given here in the form of an *R* index [$R = \sum |\nu_{\text{obs}} - \nu_{\text{calc}}| / \sum \nu_{\text{obs}}$].

For bromellite, a six-parameter VFF for interpreting the vibrational frequencies with the rigid-ion model was given by Ramani *et al.* (1976); this field includes bond-bending, bending–stretching and bending–bending contributions and the agreement with the experimental data is better than for any previous model. With application of our best-fit program to the Raman and IR data, a four-parameter VFF giving a good agreement with these data could be easily found (see Tables 1 and 2). Although the number of IR- and Raman-active frequencies to be fitted does not greatly exceed the number of constants to be derived, the agreement of these models with a considerable number of additional data, like the phonon-dispersion curves (see below), in our opinion renders them physically acceptable.

The atomic charge assigned to the O atoms in corundum or bromellite by Iishi (1978*b*) and Ramani *et al.* (1976) is 0.955 and 1.04, respectively, in electron units. In view of the similarity between these values, of the identical value of the electronegativity of Be and Al and of further application of our field to complex oxides containing both these metals, such as chrysoberyl (BeAl_2O_4), a unique value (0.97*e*) has been assigned to the O atoms in these two compounds.

With our VFF models, the phonon-dispersion curves along $[001]$ and $[2\bar{1}0]^*$ ($= [100]$) were obtained for corundum and bromellite: the latter are reported in Fig. 1. The agreement with the experimental data is satisfactory and definitely better than for any previous model; for corundum, unfortunately, no data of this kind are reported in the literature for comparison. In any case, imaginary frequencies are absent.

In Fig. 1, some ripples of the acoustic branches are reported close to the origin; they are due to the critical convergence of the Ewald sums for $q \rightarrow 0$. Hence, to obtain a correct value for the elasticity coefficients (Kittel, 1966) considerably more detailed calculations may be required; however, since the main objectives of our work are different, at least for the present time we have not insisted on developing better routines for improving our results in this respect.†

The calculated values for the a.d.p.s at different temperatures (in the form of *U* matrices, with the assumption that the frequencies are constant) are reported in Table 3, together with the corresponding

† In Table 1(*a*), some examples of the calculated elasticity coefficients are reported, together with the corresponding experimental data reported by Cline, Dunegan & Henderson (1967) for bromellite and by Gieske & Barsch (1968) for corundum; the agreement is within an order of magnitude. This table has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP55667 (2 pp.). Copies may be obtained through The Technical Editor, Interactional Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

experimental values obtained by Spackman *et al.* (1981), Lewis *et al.* (1982) and Kirfel & Eichhorn (1990) for corundum and by Pryor & Sabine (1964), Sabine & Hogg (1969), Downs *et al.* (1985) and Hazen & Finger (1986) for bromellite. The agreement is very good, especially for the most accurate experimental data.

A lattice-dynamical calculation of the Debye-Waller parameters at room temperature (300 K) was performed by Hewat (1972). According to this calculation, the parameters for the Be and O atoms should be equal ($B = 0.27 \text{ \AA}^2$), in contrast to the experimental results obtained by Downs *et al.* (1985), which are confirmed by us.

For corundum, the values at 4 K practically coincide with the zero-point motion: they amount to about 60% of the corresponding room-temperature data, a figure still higher than that for forsterite (Pilati *et al.*, 1990b).

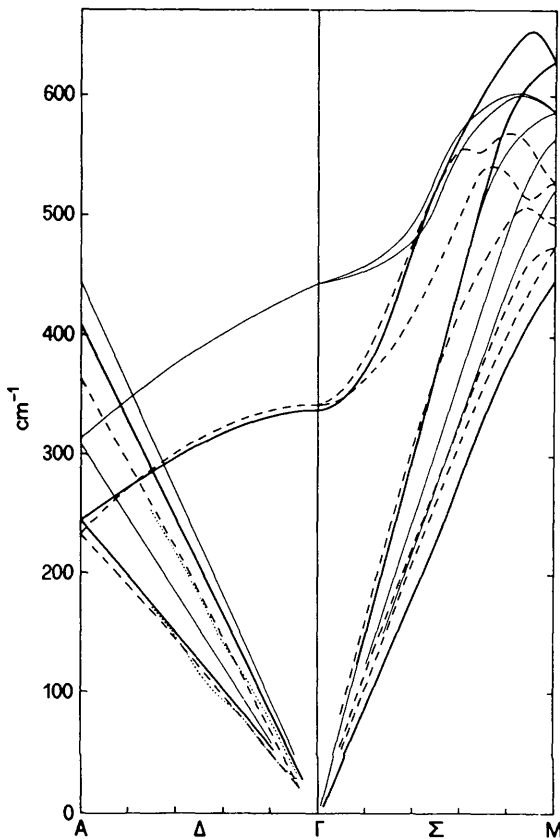


Fig. 1. Lower branches of phonon-dispersion curves for bromellite along [001] (left) and $[2\bar{1}0]^*$ (right). The heavy continuous curves are the experimental values found by Ostheller *et al.* (1968) and reported by Ramani *et al.* (1976), together with the results of their calculations (light continuous curves); our values are reported as heavy dashed curves. The ripples in proximity to the origin (light dotted curves) correspond to our calculations performed with an insufficient number of points in the reciprocal-lattice summations (max. $\sin \theta/\lambda = 0.65 \text{ \AA}^{-1}$ instead of our currently used value of 0.85 \AA^{-1}).

Together with the thermal-motion tensors U_p ($=\langle \mathbf{u}_p \mathbf{u}_p^T \rangle$), relative to the same atom p , the tensors U_{pq} ($=\langle \mathbf{u}_p \mathbf{u}_q^T \rangle$) between different atoms p and q can be calculated from lattice dynamics and thermal corrections to the experimental bond lengths can be derived in the most general case using the procedures of Scheringer (1972) or Johnson (1980) (see also Filippini & Gramaccioli, 1989; Pilati *et al.*, 1990b). For instance, for corundum at room temperature, the two shortest Al–O distances should be increased by 0.022 \AA owing to this effect.

In calculations of the values of thermodynamic functions reported in Table 4, since the experimental molar heat capacity is usually reported as c_p and our lattice-dynamical results are obtained as c_v , the well known relationship

$$c_p - c_v = \alpha^2 TV / \beta \quad (8)$$

was used to compare these data. Here, α and β are the volume thermal-expansion coefficient and the isothermal compressibility coefficient, respectively (β is the reciprocal of the so-called bulk modulus of the material):

$$\begin{aligned} \alpha &= (1/V)(\partial V / \partial T)_P \\ \beta &= -(1/V)(\partial V / \partial P)_T. \end{aligned} \quad (9)$$

In turn, β is related to the elasticity coefficients (Nye, 1957),

$$\beta = s_{11} + s_{22} + s_{33} + 2(s_{12} + s_{13} + s_{23}), \quad (10)$$

where s_{ij} are the compliances; the 6×6 matrix \mathbf{M} whose elements are the compliances is the inverse of the matrix \mathbf{C} whose components are the elastic stiffnesses (c_{ij}); for corundum both the s_{ij} and the c_{ij} are reported in the literature (Mayer & Hiedemann, 1961; Aleksandrov & Rizhova, 1961; Reddy, 1963; Gieske & Barsch, 1968). From these data, β can be estimated to be $4.74 \times 10^{-12} \text{ m}^2 \text{ N}^{-1}$; the experimental values for α as a function of temperature are given by Schauer (1965).

For bromellite, experimental data reported as c_p up to 700 K are given by Chase *et al.* (1974) and Hofmeister, Hoering & Virgo (1987); these data were obtained from the experimental measurements of c_p using (8), where the values for α as a function of temperature are given by Skinner (1966). An experimental value for β can be obtained from Cline, Dunegan & Henderson (1967); this is in good agreement with the high-pressure crystallographic data reported by Hazen & Finger (1986). For higher temperatures, we have applied the same relationship to the measured c_p data reported in the *CRC Handbook of Chemistry and Physics* (1983).

In general, there is good agreement between the calculated and the experimental values of the molar heat capacity, especially for corundum (within 1.3% between 150 and 1000 K). Since the frequencies are

Table 3. Observed and calculated atomic displacement parameters ($U \times 10^5$)

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

The values corresponding to the columns where temperature is indicated are results from our lattice-dynamical calculations. The experimental values are from the following sources.

(a) Kirfel & Eichhorn (1990): multipole refinement; synchrotron data.

(b) Spackman *et al.* (1981): multipole refinement.

(c) Lewis *et al.* (1982): multipole refinement.

(d) Hazen & Finger (1986): conventional refinement from powder neutron diffraction data.

(e) Downs *et al.* (1985): multipole refinement of single crystal γ -ray diffraction data with correction for extinction, from their model GSF.HO.

(f) Pryor & Sabine (1964): powder neutron diffraction data.

(g) Sabine & Hogg (1969): single-crystal neutron diffraction data, not corrected for extinction.

For corundum, the U tensor for oxygen here corresponds to the atom located at $x, x, \frac{1}{4}$.

Corundum	(a)	(b)	(c)	298 K	500 K	1000 K	4 K
Al U_{11}	242 (2)	319 (2)	257 (2)	278	415	786	166
U_{33}	246 (3)	325 (3)	261 (10)	259	391	739	161
$B_{eq} (\text{\AA}^2)$	0.192	0.253	0.204	0.215	0.321	0.608	0.130
O U_{11}	265 (3)	358 (4)	305 (13)	325	463	854	220
U_{12}	121 (1)	168 (5)	141 (7)	151	213	390	103
U_{13}	33 (1)	33 (3)	34 (6)	5	8	15	2
U_{33}	310 (4)	419 (4)	333 (15)	312	450	829	217
$B_{eq} (\text{\AA}^2)$	0.221	0.299	0.248	0.257	0.369	0.680	0.176
Bromellite	(d)	(e)	(f)	(g)	298 K		
Be U_{11}	553 (170)	450 (10)			390		
U_{33}	556 (93)	410 (20)			428		
$B_{eq} (\text{\AA}^2)$	0.437	0.34	0.35 (6)	0.27 (8)	0.318		
O U_{11}	304 (170)	330 (10)			312		
U_{33}	370 (93)	320 (10)			346		
$B_{eq} (\text{\AA}^2)$	0.257	0.260	0.27 (5)	0.53 (9)	0.256		

Table 4. Molar heat capacity ($J \text{ mol}^{-1} \text{ K}^{-1}$) and vibrational energy ($J \text{ mol}^{-1}$) for corundum and bromellite at various temperatures (K)

Experimental values for corundum from 4K up to room temperature from Furukawa *et al.* (1956), for higher temperatures from Robie *et al.* (1978). For bromellite, the data are taken from Chase *et al.* (1974) or from the *CRC Handbook of Chemistry and Physics* (1983) (as c_p , corrected here) for temperatures above 700 K: at room temperature, there is appreciable discrepancy between these two sources and the value corresponding to the latter is reported between parentheses.

T (K)	Corundum			Bromellite		
	c_p (obs.)	c_p (calc.)	E_{vib}	c_p (obs.)	c_p (calc.)	E_{vib}
4	0.00	0.00	44.22		0.00	21.30
50	1.51	1.34	44.27	0.17	0.25	21.30
100	12.84	12.22	44.52	2.68	2.72	21.38
150	31.97	32.05	45.61		8.33	21.63
200	51.17	51.84	47.74		15.19	22.22
298	78.99	79.87	54.27	25.40 (26.02)	26.65	24.31
500	105.98	106.06	73.35	38.41	38.99	31.13
750	118.49	117.61	101.09	44.85	44.52	41.67
1000	124.98	125.35	121.13	49.25	46.78	53.14
1250	129.16	127.44	130.42	52.93	47.86	64.98

assumed to be temperature independent, the agreement at high temperature is not so good: for instance, above 1000 K, the calculated values become appreciably smaller than the experimental values. For corundum, the calculated value of the entropy S at room temperature (298 K) is $50.75 \text{ J mol}^{-1} \text{ K}^{-1}$, compared with the experimental values of $50.96 \text{ J mol}^{-1} \text{ K}^{-1}$ (Furukawa *et al.*, 1956) and $50.83 \text{ J mol}^{-1} \text{ K}^{-1}$ (Robie *et al.*, 1978): the agreement is therefore excellent, being within the presumable range (0.33) of the standard deviation. For bromellite, the calculated value of entropy at room temperature is $14.56 \text{ J mol}^{-1} \text{ K}^{-1}$, to be compared with the experimental values of $13.77(4)$ and $14.10 \text{ J mol}^{-1} \text{ K}^{-1}$ reported by Robie *et*

al. (1978) and the *CRC Handbook of Chemistry and Physics* (1983), respectively.

For corundum and bromellite, the zero-point contributions to the vibrational energy at room temperature are 81.5 and 87.6%, respectively; these are in line with the zero-point-motion contributions to the a.d.p.s (see Table 3) and are not surprising when compared with similar results obtained for other substances (Filippini & Gramaccioli, 1989; Pilati *et al.*, 1990b).

Therefore, we have seen additional examples of derivation of thermal parameters and thermodynamic functions for crystalline substances from lattice dynamics and spectroscopic data. The agreement with

the experimental data obtained here confirms the validity of crystallographic measurements and procedures and demonstrates that it may be possible to obtain consistent empirical force fields that are useful for these purposes.

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