

the high-temperature structure of HoCu₂, suggested by Amin (1974) to be the NdAu₂-type structure (as yet undetermined), the transformation responsible for the twinning and the room-temperature lattice parameters of untwinned single crystals.

Since most REM₂ (*M* = Cu, Zn) compounds are isostructural with KHg₂, are chemically similar and exhibit massive twinning, it is probable that they exhibit the same twinning geometry as HoCu₂.

The authors acknowledge Mr Prabhat Kejriwal for preparing the alloy sample.

References

AMIN, A. A. H. (1974). MS thesis, The Pennsylvania State Univ., USA.

- CHIOTTI, P. & MASON, J. T. (1965). *Trans. Metall. Soc. AIME*, **233**, 786–795.
 CHIOTTI, P. & MASON, J. T. (1967). *Trans. Metall. Soc. AIME*, **239**, 547–552.
 CHIOTTI, P., MASON, J. T. & GILL, K. J. (1963). *Trans. Metall. Soc. AIME*, **227**, 910–916.
 DUWELL, E. J. & BAENZIGER, N. C. (1955). *Acta Cryst.* **8**, 705–710.
 HUBBARD, C. R., LEDERMAN, S. & PYRROS, N. P. (1985). *NBS-JCPDS-LSQ85*. National Bureau of Standards (now NIST), Washington, DC 20234, USA.
 KEIRI WAL, P. K. (1962). MS thesis, The Pennsylvania State Univ., USA.
 LARSON, A. C. & CROMER, D. T. (1961). *Acta Cryst.* **14**, 73–74.
 MASON, J. T. & CHIOTTI, P. (1968). *Trans. Metall. Soc. AIME*, **242**, 1167–1171.
 MICHEL, D. J. & RYBA, E. (1969). *Trans. Metall. Soc. AIME*, **245**, 436–437.
 SMETANA, Z., ŠÍMA, V. & LEBECH, B. (1986). *J. Magn. Magn. Mater.* **59**, 145–152.
 STORM, A. R. & BENSON, K. E. (1963). *Acta Cryst.* **16**, 701–702.

Acta Cryst. (1993). **B49**, 216–222

Atomic Thermal Parameters and Thermodynamic Functions for Chrysoberyl (BeAl₂O₄) from Vibrational Spectra and Transfer of Empirical Force Fields

BY TULLIO PILATI

CNR, Centro per lo Studio delle Relazioni tra Struttura e Reattività Chimica, Via Golgi 19, I-20133 Milano, Italy

FRANCESCO DEMARTIN

Istituto di Chimica Strutturistica Inorganica, Università degli Studi, Via Venezian 21, I-20133 Milano, Italy

FRANCESCO CARIATI AND SILVIA BRUNI

Dipartimento di Chimica Inorganica e Metallorganica, Università degli Studi, Via Venezian 21, I-20133 Milano, Italy

AND CARLO MARIA GRAMACCIOLI

Dipartimento di Scienze della Terra, Sezione di Mineralogia, Università degli Studi, Via Botticelli 23, I-20133 Milano, Italy

(Received 24 June 1992; accepted 2 November 1992)

Abstract

Using empirical atomic charges and valence force fields derived from a best fit to the Raman–IR spectra, and applying a rigid-ion Born–von Karman model, atomic thermal parameters have been calculated for chrysoberyl (BeAl₂O₄). The agreement with the experimental values (redetermined here for this purpose) is good; and excellent agreement with the experimental data is obtained for the estimates of some thermodynamic functions such as entropy and the molar heat. As for other oxides and silicates, the

zero-point contribution is particularly important with respect to both the vibrational energy and to the mean-square amplitude of motion (about 83 and 70% of the value at room temperature, respectively). In order to test transferability of the force fields, the vibrational frequencies have also been calculated using empirical valence force-field parameters derived from a best fit to the Raman–IR spectra of corundum (Al₂O₃) and bromellite (BeO), without fitting the chrysoberyl spectra. The agreement with the experimental values is good, especially for the low frequencies. However, there is significant dis-

agreement for the higher frequencies, which apparently require larger stretching-force constants than for both corundum and bromellite: these constants also appear to be more dependent upon bond distance (especially for the Be—O bonds). This behaviour may reflect some inadequacy of the rigid-ion model used here for these calculations. However, the agreement with the experimental atomic thermal parameters and thermodynamic functions is good, because the lowest energy vibrational levels (corresponding to the softest modes, including the acoustic branches near the origin of the Brillouin zone) are the most important for these applications.

Introduction

The problem of interpreting the vibrational spectra of solids is interesting, not only for advancement in infrared or Raman spectroscopy, but also for examining the possibility of deriving thermodynamic functions and atomic thermal parameters (see, for instance, Willis & Pryor, 1975; Price, Parker & Leslie, 1987*a*; Gramaccioli, 1987; Pilati, Bianchi & Gramaccioli, 1990*a*; Pilati, Demartin & Gramaccioli, 1993).

There are a number of works on this subject; they are essentially limited to the evaluation of thermodynamic functions following the Debye model implemented by the contribution of the optic modes (Kieffer, 1979*a,b,c*, 1980, 1982, 1985; Hofmeister, Hoering & Virgo, 1987). In these works, an empirical force field is generally derived by fitting the measured frequencies of a certain substance (especially Raman or infrared spectra) or of a group of similar substances: here, a very important point to be clarified is the transferability of the force field to other compounds. For entire groups of molecules, especially organic molecules, this has long been shown to be a valid possibility (see, for instance, Schachtschneider & Snyder, 1963; Snyder & Schachtschneider, 1965; Neto, Scrocco & Califano, 1966; Califano, 1976). The same has also been found for some groups of crystals formed by uncharged molecules (see, for instance, Gramaccioli, 1987; Filippini & Gramaccioli, 1989, and references therein).

For these reasons, and in agreement with other authors (Price, Parker & Leslie, 1978*b*) we wondered whether (and up to what level of accuracy) transferability of force fields could hold even for non-molecular substances with charged atoms, such as oxides or oxy salts. For many such substances (which are very well represented by the known minerals) spectroscopic data are frequently reported in the literature. Unfortunately, most of these data were not derived from accurate measurements on single crystals, and there are surprisingly few works where reliable symmetry labelling of the modes is

Table 1. *Crystal data (present sample)*

Space group	<i>Pnma</i>
<i>Z</i>	4
<i>a</i>	9.4019 (9) Å
<i>b</i>	5.4746 (3) Å
<i>c</i>	4.4259 (2) Å
Density (measured)	3.69 g cm ⁻³
(calculated)	3.700 g cm ⁻³
Refractive indices	<i>n_x</i> = 1.740 = <i>c</i>
	<i>n_y</i> = 1.741 = <i>a</i>
	<i>n_z</i> = 1.749 = <i>b</i>
Colour	Lilac with strong pleochroism
No. of reflections used in the refinement	482
Final <i>R</i> value	0.0116
<i>wR</i>	0.0116

given. Still fewer are the cases where phonon-dispersion curves have been measured by inelastic neutron scattering. Now that reliable procedures are being developed for routine calculations of vibrational spectra in crystals (see Pilati, Bianchi & Gramaccioli 1990*a,b,c*), the lack of good experimental data has become the major obstacle for extending considerations of this kind.

Following our gemmological interest in chrysoberyl (Sosso, Soi, Pilati, Diella, Liborio & Gramaccioli, 1989), a sample of synthetic alexandrite, a variety containing small amounts of Cr₂O₃ and Fe₂O₃ (0.4 and 0.1% by weight, respectively) was obtained from Istituto Gemmologico Italiano and cut perpendicular to its crystallographic axes by Mr Benito Piacenza: its properties are reported in Table 1. This sample was particularly suitable for good measurements of physical properties because of its excellent quality. At the same time, in line with the general problem stated above, if good spectral data on chrysoberyl are obtained, then it should be interesting to interpret them using the empirical force fields concerning the Al—O and Be—O bonds already derived for corundum or bromellite (BeO) (Iishi, 1978; Pilati, Demartin & Gramaccioli, 1993) where the coordination of the metal atoms is identical to the corresponding atoms in chrysoberyl. Therefore, the possibility of transferring these empirical fields to other substances can be verified.

A Urey—Bradley force field has been successfully used by Iishi (1978) to interpret the Raman- and infrared-active vibrational frequencies of corundum, and to provide reasonable estimates of the elasticity coefficients. A valence force field (VFF) for corundum which provides a good fit with the experimental Raman and infrared spectral data, as well as to the atomic thermal parameters and thermodynamic functions, has also been derived (Pilati, Demartin & Gramaccioli, 1993). Similarly, for bromellite a VFF involving six parameters has been successfully employed in lattice dynamics by Ramani, Mani & Singh (1976), whereas a four-parameter VFF almost matching the experimental frequencies (including the phonon dispersion curves) has been derived by Pilati,

Table 2. *Empirical valence force fields used*

(1) Field derived from corundum and bromellite (Pilati *et al.*, 1993) without any fit to chrysoberyl data. (2) Field as above, with readjustment of stretching constants to fit the highest frequencies of chrysoberyl. (3) Field derived from best fit to chrysoberyl data. (4) Since the electron charge is negative, here negative numbers correspond to positive charge. 1 dyn = 1×10^{-5} N.

Stretching force constants in the form: $A + B(d - d_0)$			
	A (mdyn \AA^{-1})	B (mdyn \AA^{-2})	d_0 (\AA)
Al—O	1.404	-1.581	1.914 (1)
	1.464	-3.461	1.914 (2)
	1.572	-5.407	1.914 (3)
Be—O	1.897		1.637 (1)
	2.252	-10.764	1.637 (2)
	2.555	-8.538	1.637 (3)
Bending force constants (mdyn $\text{\AA} \text{ rad}^{-2}$)			
O—Al—O		0.54318	(1)–(2)
		0.32273	(3)
O—Be—O		0.21555	(1)–(2)
		0.30420	(3)
Al—O—Be		0.34747	(3)
Stretching–stretching constants (mdyn \AA^{-1})			
Al—O bonds centred on the same Al atom			-0.01675 (1)–(2)
			0.18386 (3)
Be—O bonds centred on the same Be atom			0.06812 (1)–(2)
			0.43519 (3)
Stretching–bending constants (mdyn rad^{-1})			
Bonds and angles centred on the same Al atom			0.16615 (1)–(2)
			0.12170 (3)
Bonds and angles centred on the same Be atom			0.08536 (1)–(2)
			0.23642 (3)
Bonds and Al—O—Be angles centred on the same O atom			0.05160 (3)
Bending–bending force constants (mdyn $\text{\AA} \text{ rad}^{-2}$)			
O—Al—O angles sharing a side			-0.02557 (1)–(2)
O—Al—O angles sharing the Al atom only			-0.06766 (1)–(2)
Atomic charge (in electron units) (4)			
O	0.97	Be	-0.97
O	0.854	Be	-0.735
		Al	-1.455 (1)–(2)
		Al	-1.340 (3)

Demartin & Gramaccioli (1993). Data regarding the force fields used here are reported in Table 2.

Because of the frequent occurrence of excellent natural crystals of beryllium minerals, many of which are well known gems, such as beryl $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, phenakite Be_2SiO_4 , euclase BeAlSiO_4 -(OH) *etc.*, there are particularly favourable opportunities for good measurements of vibrational spectra. This further justifies our choice of chrysoberyl as one of the first substances to be examined for checking the transferability of force fields. A similar interest in examining a group of beryllium minerals, especially concerning the values of the thermodynamic functions obtained by using a modified Debye procedure implemented with partially interpreted Raman and infrared spectral data, has been shown by Hofmeister, Hoering & Virgo (1987).

Experimental measurements

Measurements of Raman and infrared spectra for chrysoberyl have been made by two of us (FC and SB) at room temperature using a CODERG PHO Raman spectrophotometer and a BIO-RADD

FTS-40 Fourier-transform infrared spectrophotometer. The reflection infrared data were elaborated using a Kramers–Krönig analysis (Poulet & Mathieu, 1970). The results are reported in the first column of Table 3, where they are compared with similar measurements obtained by Weiyi *et al.* (1985) for Raman data or by us in transmission infrared spectroscopy, and by Burshtein, Henderson, Morgan & Silberman (1989): these results are reported in the second and third columns of Table 3, respectively.

Experimental estimates for the thermal factors for chrysoberyl at room temperature and pressure reported in the literature show extensive mutual (and systematic) disagreement, exceeding at least 40% of the values (Farrell, Fang & Newham, 1963; Hazen, 1987; Hazen & Finger, 1987). The reason for this can very probably be ascribed to the effect of secondary extinction (Downs, Ross & Gibbs, 1985). Accordingly, a refinement of the crystal structure has been carried out, collecting a new data set from a very small splinter ($0.05 \times 0.05 \times 0.10$ mm) of the same sample we had used for measuring Raman and infrared spectra, mounted on an Enraf–Nonius CAD-4 diffractometer. 25 intense reflections, having a θ value in the range 18 – 20° , were centred using graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Least-squares refinement of their setting angles resulted in the unit-cell parameters reported in Table 1. The orientation matrix relating the crystal axes to the diffractometer axes was also obtained in this way. A total of 1471 diffracted intensities were collected at room temperature (298 K) with variable scan speed (maximum scan time for each reflection: 90 s) by exploring the quadrants of the reciprocal lattice with $-17 < h < 17$, $0 < k < 9$ and $0 < l < 8$ out to a maximum 2θ angle of 80° . The diffracted intensities were corrected for Lorentz–polarization and background effects.

An empirical absorption correction was applied according to North, Phillips & Mathews (1968); transmission factors were in the range 0.94–1.00. After averaging the symmetry-related data, which had an agreement of 0.9% based on F_o , 757 independent reflections were obtained. Of these, only 482 with $I > 3\sigma(I)$ and $\theta > 20^\circ$ were considered in the structure refinement. Scattering factors for neutral atoms and anomalous-dispersion corrections for scattering factors were taken from Cromer & Waber (1974) and Cromer (1974), respectively.

The final cycles of refinement were carried out by full-matrix least squares, minimizing the function $\sum w(F_o - k|F_c|)^2$. Weights assigned to individual observations were $1/\sigma^2(F_o)$, where $\sigma(F_o) = [\sigma^2(I) + (kI)^2]^{1/2}/2F_oLp$, $\sigma^2(I)$ is the standard deviation for each reflection as derived from counting statistics, k (=0.005) is a coefficient for improving the goodness of fit and Lp is the Lorentz–polarization factor. The

Table 4. Fractional atomic coordinates with e.s.d.'s in parentheses

	x	y	z
Al(1)	0	0	0
Al(2)	0.27283 (2)	$\frac{1}{2}$	-0.00506 (5)
Be	0.0928 (1)	$\frac{1}{2}$	0.4339 (2)
O(1)	0.09034 (5)	$\frac{1}{2}$	0.7877 (1)
O(2)	0.43300 (4)	$\frac{1}{2}$	0.2414 (1)
O(3)	0.16329 (3)	0.01543 (6)	0.25688 (8)

extinction correction was applied according to the formula $|F_o| = |F_c|/(1 + gIc)$ with $g = 2.4 \times 10^{-5}$. All the calculations in this structure-refinement procedure were performed on a PDP11/73 computer using the *SDP-Plus Structure Determination Package* (B. A. Frenz & Associates Inc., 1980). The maximum residual in the final difference Fourier synthesis was $0.2 \text{ e } \text{\AA}^{-3}$, and final R and wR indices were 0.0116 and 0.0116, respectively. The final atomic coordinates (with their e.s.d.'s) are listed in Table 4, thermal parameters in Table 5.*

Calculation procedure and discussion

In our calculations, we have used the same procedures and computing programs as for fosterite Mg_2SiO_4 , with the methods we have used for corundum and bromellite (Pilati, Bianchi & Gramaccioli, 1990*a,b,c*; Pilati, Demartin & Gramaccioli, 1993) for improving the fit with observed frequencies and for dealing with an infinite network of bond angles extending throughout the crystal.

In the fourth column of Table 3 the calculated vibrational frequencies for chrysoberyl at the origin of the Brillouin zone ($q = 0$) are reported. Here the parameters of the empirical VFF are those derived from a best fit to corundum and bromellite only, without considering the corresponding data for chrysoberyl; these parameters correspond to field (1) in Table 2.

The agreement with the strongest measured peaks is remarkably good, especially for the lower frequencies. Those at higher frequencies are clearly estimated to be too low. A much better agreement with the experimental data is given by modifying the stretching-force constants (especially those relative to Be—O bonds) and their dependence upon bond length. This field is designated (2) in Table 2, and the corresponding calculated Raman- and infrared-active vibration frequencies are reported in the fifth column in Table 3.

* A list of observed and computed structure-factor moduli have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55691 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0439]

Table 5. Atomic displacement parameters (U 's $\times 10^5$)

Observed values from our X-ray crystal structure refinement. Z.p. = zero-point contribution. Our experimental data are about 15% smaller than the corresponding data reported by Hazen & Finger (1987) and about 50% smaller than the data reported by Hazen (1987). The calculated values are reported in sequence, using our force fields (1), (2) and (3) specified in Table 2. The temperature factor expression is in the form: $T = \exp\{-2\pi^2[U_{11}(ha^*)^2 + \dots + 2U_{23}kb^*c^*]\}$.

	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}	$B_{2a}(\text{\AA}^2)$
Al(1)	Obs. 360 (5)	-40 (5)	10 (6)	292 (6)	-16 (6)	328 (5)	0.258 (2)
	Cal. 330	-19	-14	288	-12	322	0.247
	315	-21	-8	271	-11	296	0.232
	Z.p. 182	-9	-3	162	-5	175	0.137
Al(2)	Obs. 302 (5)	0	-6 (6)	364 (6)	0	336 (6)	0.264 (2)
	Cal. 259	0	21	311	0	299	0.229
	253	0	14	304	0	291	0.223
	Z.p. 155	0	7	179	0	174	0.134
Be	Obs. 580 (20)	0	20 (20)	520 (20)	0	420 (20)	0.400 (10)
	Cal. 448	0	-6	445	0	390	0.338
	451	0	7	418	0	340	0.318
	Z.p. 336	0	5	312	0	261	0.239
O(1)	Obs. 370 (10)	0	20 (10)	370 (10)	0	280 (10)	0.270 (5)
	Cal. 343	0	0	345	0	317	0.265
	336	0	5	326	0	281	0.248
	Z.p. 227	0	4	223	0	195	0.170
O(2)	Obs. 330 (10)	0	-60 (10)	400 (10)	0	370 (10)	0.290 (5)
	Cal. 318	0	-10	353	0	339	0.266
	311	0	2	339	0	323	0.256
	Z.p. 213	0	0	230	0	221	0.175
O(3)	Obs. 390 (8)	36 (8)	-34 (9)	379 (9)	30 (10)	368 (8)	0.299 (3)
	Cal. 346	15	-5	333	-2	341	0.269
	342	23	-12	326	-5	330	0.262
	Z.p. 230	14	-5	220	-4	227	0.178

However, there is still significant disagreement for some of the lowest frequencies. For instance, in the observed infrared spectrum minor peaks are present at 325 and 291 cm^{-1} with B_{1u} and B_{2u} symmetry, respectively. These peaks cannot be compared with our calculated values and have also been observed in the transmission spectrum. Similarly, in the Raman spectrum there are two weak peaks at 352 and 365 cm^{-1} which have B_{2g} symmetry, instead of one as expected according to our force fields (1) and (2). To examine the possibility of a better interpretation of the low-frequency experimental data, a force field was also derived from a best fit to the chrysoberyl spectra using 15 different parameters, and in the minimization procedure a weight, inversely proportional to the fourth power of the frequency, was assigned. This field is indicated as (3) in Table 2, and the calculated frequencies relative to it are reported in the last column of Table 3. For all the fields considered here, no imaginary frequencies are observed in the whole Brillouin zone.

Estimates of the atomic thermal parameters (as U 's) are reported in Table 5. For each atom, the first line corresponds to our experimental data, the second shows the results of our calculations using the field fitted to corundum and bromellite spectral data without modifications [(1) in Table 2], the third line

Table 6. Bond distances (Å) for chrysoberyl

The second column shows data corrected for thermal vibration; e.s.d.'s are given in parentheses.

	Uncorrected	Corrected
Al(1)—O(1)	1.865 (1)	1.868
Al(1)—O(2)	1.892 (1)	1.894
Al(1)—O(3)	1.912 (1)	1.915
Al(2)—O(1)	1.945 (1)	1.947
Al(2)—O(2)	1.860 (1)	1.862
Al(2)—O(3)	1.893 (1)	1.895
Al(2)—O(3)	2.013 (1)	2.015
Be—O(1)	1.566 (1)	1.570
Be—O(2)	1.691 (1)	1.694
Be—O(3)	1.644 (1)	1.647

shows the results obtained from the force field fitted to the chrysoberyl spectral data [(2) in Table 2], the fourth line shows the results from our 15-parameter best-fit field [(3) in Table 2], and the fifth line shows the zero-point contribution [using field (2)]. The difference between the corresponding results of these force fields is relatively small, and the agreement with the experimental data is always substantially good. As for corundum, bromellite and forsterite, the zero-point contribution is remarkable, ranging from about 60% of the total for the aluminium atoms at room temperature up to 75% for the beryllium atom.

Since lattice dynamics provides all the necessary tensors for thermal-motion correction of the experimental bond distances (see, for instance, Pilati, Bianchi & Gramaccioli, 1990*a,b,c*; Pilati, Demartin & Gramaccioli, 1993), in Table 6 the bond distances obtained from our structure refinement are reported, together with their corrected values: as in similar cases, the correction at room temperature is small, being of the order of 0.002–0.003 Å.

Calculated values of thermodynamic functions (entropy and the molar heat capacity c_p) are reported in Table 7, together with the corresponding experimental data and with an estimate of the total vibrational energy. Since the reported experimental data for the molar heat are given as c_p , and our calculations provide estimates for c_v , the well known relationship:

$$c_p - c_v = \alpha^2 TV / \beta$$

has been used. Here α and β are the volume thermal expansion coefficient and the isothermal compressibility coefficient, respectively:

$$\alpha = 1/V(\delta V/\delta T)_P; \quad \beta = -1/V(\delta V/\delta P)_T.$$

For α , the estimate ($= 13.8 + 0.011T \mu\text{K}^{-1}$) reported by Hofmeister, Hoering & Virgo (1987) can be adopted, in line with the data reported by Fizeau (1888) and by Geller, Yavorsky, Steierman & Creamer (1946). This estimate is surely inadequate for the lowest temperatures, since it is not zero at 0 K as it should be according to theory. However,

since the difference $c_p - c_v$ is quite small, even assuming an error of 50% in α , the resulting error in calculating c_p would be about 2% at 50 K and 0.5% at 100 K. For β , which is the reciprocal of the so-called 'bulk modulus' of the material, a value of $4.2 \times 10^{-13} \text{ cm}^2 \text{ dyn}^{-1}$ ($1 \text{ dyn} = 1 \times 10^{-5} \text{ N}$) can be deduced using Hazen's (1987) data, in agreement with Cline, Dunegan & Henderson (1967). Hence the calculated values for c_p reported in Table 7.

The agreement with the experimental values is very good: using force field (3) it is within 2.2% for c_p from 0 to 700 K, and for the entropy S it is within 1.1% between 150 and 700 K; if field (2) is used, the agreement is only slightly worse. At least at room temperature, there is reasonable agreement (within 4.2%) even using field (1) transferred from bromellite and corundum, without any fit to the chrysoberyl spectral data. At the highest temperatures, the calculated values are systematically smaller than the corresponding experimental values: this is because in our calculations the vibrational frequencies are assumed to be constant with respect to variations of temperature. A similar result has been obtained for corundum (Pilati, Demartin & Gramaccioli, 1993).

On comparing the results obtained using force fields (1) and (2), the above situation can be explained, at least in part, on account of the overwhelming prevalence of the lowest vibrational energy levels in determining the values of both thermodynamic functions and thermal parameters (see, for instance, Pilati, Demartin & Gramaccioli, 1993). Therefore, variations of the bond-stretching constants (which are especially effective upon the highest frequencies) are not relevant under this consideration. At the same time, one might wonder why the force-field constants affecting the lower frequencies are transferable, whereas the others are not. Since the rigid-ion model, used here, is known to work particularly well for lower frequencies only (see, for instance, Woods, Cochran & Brockhouse, 1960; Cochran, 1973; Ghose, 1985; Pilati, Demartin, & Gramaccioli, 1993), the supposed lack of transferability may be due to inadequacy of the model, and no conclusions about this argument can be drawn on these grounds; another possibility is that the bromellite frequencies are too few to establish a physically reliable force field for the Be—O bonds.

Another problem concerns a comparison between force fields (2) and (3): here the difference is substantial in all respects, and even the lower frequencies can be different, as well as the values of the bending constants, *etc.* On these grounds, it is difficult to consider the force field to be really transferable. However, as we have seen, field (3) has been derived in order to account for two or three weak low-frequency peaks in the spectrum: there is some possibility that these low frequencies may be a result of

Table 7. *Thermodynamic functions at 1 atm as a function of temperature* [c_p and S in $\text{cal mol}^{-1} \text{K}^{-1}$, E_{vib} in cal mol^{-1} (1 cal = 4.184 J)]

The force field is fitted to chrysoberyl spectral data. Corresponding estimates using the force fields derived from corundum and bromellite are given in parentheses. Experimental data for $T < 500$ K from Furukawa & Saba (1965); for higher values of T from Hemingway, Barton, Robie & Haselton (1986).

T (K)	c_p			S			E_{vib}	
	Obs.	Cal. (2)	Cal. (3)	Obs.	Cal. (2)	Cal. (3)	(2)	(3)
4	0.00	0.00	0.00	0.00	0.00	0.00	15.82	15.90
50	0.47	0.43	0.46	0.14	0.03	0.03	15.83	15.90
100	3.91	3.82	3.95	1.32	1.19	1.25	15.92	15.99
150	9.80	9.94	10.02	3.98	3.84	3.95	16.25	16.33
200	15.88	16.19	16.16	7.65	7.56	7.67	16.90	16.99
250	21.10	21.44	21.35	11.77	11.73	11.83	17.84	17.92
298	25.19	25.40	25.29	15.85	15.82	15.91	18.96	19.04
		(26.12)			(16.52)			
500	34.88	34.52	34.44	31.56	31.41	31.43	25.12	25.17
700	38.90	38.16	38.11	44.01	43.52	43.52	32.34	32.38
1000	41.60	40.76	40.73	58.40	57.30	57.30	43.96	43.99
1300	43.08	42.41	42.39	69.52	67.82	67.80	55.98	56.00

forbidden lattice modes connected with the presence of impurities, or a possible overtone for the $365 \text{ cm}^{-1} B_{2g}$ peak, and in this case the better agreement with the experimental data would be negligible. Alternatively, as we have seen, our field (3) provides the best agreement with both thermodynamic functions and atomic thermal parameters (see Tables 5 and 7).

Therefore, a systematic test of these procedures and empirical functions on several different compounds is necessary: further work is in progress concerning other beryllium–oxygen compounds, which it is hoped, will provide a clearer answer to these problems.

The authors are grateful to Istituto Gemmologico Italiano for help in providing the sample studied, and to Mr Benito Piacenza and Dr Federico Sosso for having cut it appropriately. Financial assistance and equipment for our investigations have been provided by Consiglio Nazionale delle Ricerche. FC and SB wish to thank the CNR Centro di Studio sulla Sintesi e la Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione for the availability of the CODERG PHO instrument.

References

B. A. FRENZ & ASSOCIATES INC. (1980). *SDP-Plus*. Version 1.0. Enraf–Nonius, Delft, The Netherlands.
 BURSHTIN, Z., HENDERSON, D. O., MORGAN, S. & SILBERMAN, E. (1989). *J. Phys. Chem. Solids*, **50**, 1095–1100.
 CALIFANO, S. (1976). *Vibrational States*. London: John Wiley.
 CLINE, C. F., DUNEGAN, H. L. & HENDERSON, C. W. (1987). *J. Appl. Phys.* **38**, 1944–1948.
 COCHRAN, W. (1973). *The Dynamics of Atoms in Crystals*. London: Arnold.
 CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 DOWNS, J. W., ROSS, F. K. & GIBBS, G. V. (1985). *Acta Cryst.* **B41**, 425–431.
 FARRELL, E. F., FANG, G. H. & NEWNHAM, R. E. (1963). *Am. Mineral.* **48**, 804–810.
 FILIPPINI, G. & GRAMACCIOLI, C. M. (1989). *Acta Cryst.* **A45**, 261–263.
 FIZEAU, H. (1888). *Annuaire pour l'an Paris*. Paris: Bureau des longitudes.
 FURUKAWA, G. T. & SABA, W. G. (1965). *J. Res. Natl Bur. Stand.* **69A**, 13–18.
 GELLER, R. F., YAVORSKY, P. J., STEIERMAN, B. L. & CREAMER, A. S. (1946). *J. Res. Natl Bur. Stand.* **36**, 277.
 GHOSE, S. (1985). *Reviews in Mineralogy*, Vol. 14, *Microscopic to Macroscopic*, edited by S. W. KIEFFER & A. NAVROTSKY, pp. 127–163. Washington, DC: Mineralogical Society of America.
 GRAMACCIOLI, C. M. (1987). *Int. Rev. Phys. Chem.* **6**, 337–349.
 HAZEN, R. M. (1987). *Phys. Chem. Miner.* **14**, 13–20.
 HAZEN, R. M. & FINGER, L. W. (1987). *Phys. Chem. Miner.* **14**, 426–434.
 HEMINGWAY, B. S., BARTON, M. D., ROBIE, R. A. & HASELTON, H. T. JR (1986). *Am. Mineral.* **71**, 557–568.
 HOFEISTER, A. M., HOERING, T. G. & VIRGO, D. (1987). *Phys. Chem. Miner.* **14**, 205–224.
 IISHI, K. (1978). *Phys. Chem. Miner.* **3**, 1–10.
 KIEFFER, S. W. (1979a). *Rev. Geophys. Space Phys.* **17**, 1–19.
 KIEFFER, S. W. (1979b). *Rev. Geophys. Space Phys.* **17**, 20–34.
 KIEFFER, S. W. (1979c). *Rev. Geophys. Space Phys.* **17**, 35–59.
 KIEFFER, S. W. (1980). *Rev. Geophys. Space Phys.* **18**, 862–886.
 KIEFFER, S. W. (1982). *Rev. Geophys. Space Phys.* **20**, 827–849.
 KIEFFER, S. W. (1985). *Reviews in Mineralogy*, Vol. 14, *Microscopic to Macroscopic*, edited by S. W. KIEFFER & A. NAVROTSKY, pp. 65–126. Washington, DC: Mineralogical Society of America.
 NETO, N., SCROCCO, M. & CALIFANO, S. (1966). *Spectrochim. Acta*, **22**, 1981–1998.
 NORTH, A. C., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
 PILATI, T., BIANCHI, R. & GRAMACCIOLI, C. M. (1990a). *Acta Cryst.* **B46**, 301–311.
 PILATI, T., BIANCHI, R. & GRAMACCIOLI, C. M. (1990b). *Acta Cryst.* **A46**, 309–315.
 PILATI, T., BIANCHI, R. & GRAMACCIOLI, C. M. (1990c). *Acta Cryst.* **A46**, 485–489.
 PILATI, T., DEMARTIN, F. & GRAMACCIOLI, C. M. (1993). *Acta Cryst.* **A49**. In the press.
 POULET, H. & MATHIEU, J. P. (1970). *Spectres de Vibration et Symétrie des Cristaux*, pp. 171–177. Paris: Gordon & Breach.
 PRICE, G. D., PARKER, S. & LESLIE, M. (1987a). *Phys. Chem. Miner.* **15**, 181–190.
 PRICE, G. D., PARKER, S. & LESLIE, M. (1987b). *Mineral. Mag.* **51**, 157–170.
 RAMANI, R., MANI, K. K. & SINGH, R. P. (1976). *Phys. Rev. B*, **14**, 2659–2663.
 SCHACHTSCHNEIDER, J. H. & SNYDER, R. G. (1963). *Spectrochim. Acta*, **19**, 117–168.
 SNYDER, R. G. & SCHACHTSCHNEIDER, J. H. (1965). *Spectrochim. Acta*, **21**, 169–195.
 SOSSO, F., SOI, V., PILATI, T., DIELLA, V., LIBORIO, G. & GRAMACCIOLI, C. M. (1989). *Gemmologia*, **14**(3), 7–21.
 WEIJI, J., QINGRONG, ZH., YUSHENG, SH., YANYUN, W., ZHENYI, Y., SHOUAN, H., HETIAN, ZH. & LILING, L. (1985). *Kexue Tongbao*, **30**, 452–456.
 WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*. Cambridge Univ. Press.
 WOODS, A. D. B., COCHRAN, W. & BROCKHOUSE, B. N. (1960). *Phys. Rev.* **119**, 980–999.