

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.

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

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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</i> _α = 1.740 = <i>c</i>
	<i>n</i> _β = 1.741 = <i>a</i>
	<i>n</i> _γ = 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. $1 \text{ dyn} = 1 \times 10^{-9} \text{ N}$.

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)
Al—O—Be		0.30420	(3)
		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)
Bonds and Al—O—Be angles centred on the same O atom			0.23642 (3)
			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	Al -1.455 (1)–(2)
O	0.854	Be -0.735	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 ($0.05 \times 0.05 \times 0.10 \text{ mm}$) 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 $18\text{--}20^\circ$, 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 $\sigma(F_o) = [\sigma^2(I) + (kI)^2]^{1/2}/2F_oL_p$, $\sigma^2(I)$ 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 L_p is the Lorentz–polarization factor. The

Table 3. *Observed and calculated vibrational frequencies at the origin of the Brillouin zone (cm⁻¹)*

(1) Our measured data. (2) Raman data (A_g to B_{3g}) measured by Weiji *et al.* (1985); infrared data (B_{1u} to B_{3u}) measured by us in transmission. (3) Data measured by Burshtein *et al.* (1989). (4) Our calculations, using a force field derived from a fit to corundum and bromellite [(1) in Table 2]. (5) Our calculations, using our force field (2) in Table 2. (6) Our calculations, using our 'best-fit' field to chrysoberyl [(3) in Table 2].

	(1)	(2)	(3)	(4)	(5)	(6)		(1)	(2)	(3)	(4)	(5)	(6)		
A_g	245	232	243	244	250	252	B_{2u}	291	289	290	318	334	310		
	351	340	351	370	376	353		357	358	365	337	357	357	365	
	372	361	372	398	393	382			410 (?)		386	396	386	386	
	461	451	461.5	421	427	437		442	441	445	443	463	429	429	
	481	469	480	452	472	488		504		512	482	475	478	478	
	528	515	526	539	542	539		548		550	513	530	521	521	
	640	631	641	606	618	619		571	572	572	553	557	542	542	
	679	668		642	658	699		606	607	607	579	592	588	588	
	713	703	713	676	708	779		(644)	(645)	(646)					
	782	771	780	750	767	796		721		745	684	743	745	745	
	932	925	935	769	914	911									
									$B_{2u}LO$	293		295	318	334	311
					358	344		313		382		380	337	357	368
		399	387	398.5	362	378		406					387	397	391
	449	437	448.5	417	432	448	451			455	464	468	438		
	505	494	504.5	481	484	470	523			522	507	511	507		
	523	(513)		523	538	556	563			560	543	556	539		
		(642)					600			600	560	589	574		
	658	648	658	587	612	671	615			617	587	597	603		
	820	810	820	811	846	817	(660)			(665)					
							966			965	898	933	875		
B_{2g}							B_{3u}				200	198	194		
	352	335	347	297	309	325					(240)				
	365	353	363.5	338	345	346					(267)				
	424	412	422.5	413	405	407									
	437	426	436.5	422	420	441									
	(461)							375	371	385	367	378	365		
	521	509	520	508	533	525		424	420?	427	406	419	421		
	550	539	550	556	559	560					453	469	477		
		(555)						488		490	473	489	492		
	642	634	646	625	619	641		506		517	520	531	530		
	779	768		647	719	777		538	533	(572)	548	559	541		
				720	741	818				602	588	581	597		
	836	825	834	790	836	819		598		619	645	635			
	933	929		837	921	916		619		665	667	647	696	647	
						714		669		717	720	704			
						(741)						750			
						754		757	730	735	789				
						(781)		777	770						
						957		970		921	915				
B_{3g}	241	226	237.5	236	240	228	$B_{3u}LO$				201	199	195		
	357	346	357	385	397	384					(250)				
	443	431	442	452	461	438					(272)				
	482	470	480.5	471	470	471									
	569	557	567.5	546	551	553									
	680	668	678.5	604	642	684									
	747	735	746.5	773	807	795									
B_{1u}								386		390	367	378	366		
	325	324	330	263	267	295		449	447	420	430	432			
	359	358	365	373	387	370				454	471	479			
	374	371		407	403	380		500		502	487	501			
	444	441	445	442	456	455		536		540	542	541			
				492	500	496		565		565	549	565			
	521		532	503	514	521		609		617	603	600			
	550	557	555	534	548	541		665		665	625	661			
	561		572	558	560	565		685		685		713			
	606	607		573	589	586		717				731			
	638		645	611	658	682		(750)			675	789			
	773	775	777	709	717	764		779		765	727	901			
	904	909	905	742	877	843		(937)		950	766	932			
	941		940	892	922	912		974			917	932			
$B_{1u}LO$							A_u				202	200	181		
	328		335	263	267	296						314	334	310	
	364		375	373	388	371						343	355	346	
	384			408	403	382						377	377	374	
	453			442	456	456						435	449	445	
				503	512	521						450	473	487	
	542		542	532	544	541						483	486	488	
	556		565	555	551	548						534	551	566	
	604		602	562	580	571						609	626	578	
	621			601	655	671						736	782	769	
	716		685	643	682	683									
	812		815	710	718	764									
	914		960	888	883	846									
	1099		1110	918	1039	993									

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}	$B_{eq}(\text{\AA}^2)$
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
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
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
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
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
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 cal mol⁻¹ 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 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.

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