Single-crystal Vibrational Spectra of Beryl and Dioptase

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Using oriented single crystals of beryl and dioptase, almost the full number of bands predicted by factor-group analysis has been observed in each case. The same $[Si_6O_{18}]^{12-}$ ring occurs in both minerals; in dioptase, slight distortions caused by the need to provide Cu^{2+} with a tetragonal environment have a profound effect on the spectrum which bears little resemblance to that of beryl. The bonding in both crystals is discussed.

IN recent years study of the vibrational spectra of solids by methods of single-crystal physics has shown that in many cases the full number of active modes predicted by factor-group analysis (f.g.a.) can be observed. As a natural extension of this work we have investigated the spectra of two minerals with a large number of atoms in the primitive unit cell. Beryl, $Be_3Al_2Si_6O_{18}$, has two $[Si_6O_{18}]^{12-}$ rings per cell, and it was of interest to determine whether vibrational interactions between them are strong enough to generate the full spectrum, or whether a one-ring model is adequate and, indeed, whether vibrational interactions within such a large ring are sufficient to show all the possible ring vibrations. The same type of ring is present in dioptase, $Cu_6Si_6O_{18},6H_2O$: Cu^{2+} cannot occupy octahedral interstitial sites, as does Al^{3+} in beryl; accordingly the rings are slightly distorted so that copper may form four short bonds (1·96 Å) to neighbouring rings. Since dioptase has a unimolecular cell, it is an excellent system in which to investigate the effect on the ring spectrum of this relatively slight distortion and to compare the spectrum with that of beryl. Some i.r. and Raman data have been published for powder specimens of these minerals, but none of it is particularly complete. During the course of our work, an i.r.-reflectance study of beryl was reported,[1] but our study extends to lower frequencies and is essentially complete. No single-crystal work has been reported for dioptase.

EXPERIMENTAL

A colourless and optically perfect specimen of beryl of hexagonal cross-section and of unknown origin was obtained from the Geology Department, University of Leicester. Each face parallel to the *c* axis was *ca.* 10 × 3 mm². Raman spectra were obtained with a Coderg T800 triple-monochromator instrument using 488·0 nm excitation. I.r.-reflectance spectra were obtained as described previously.[2] A small crystal of dioptase (from the Djoué mine, Brazzaville, Zaire; BM no. 1927 1226) was obtained from the British Museum (Natural History); it was too small for i.r.-reflectance data of good quality to be obtained but at least the more-intense bands were found (see text). Raman spectra were excited with 514·5 nm radiation.

Selection Rules.—Beryl crystallises in the hexagonal system with the symmetry of space group $P6/mcc \equiv D_{6h}^2$ with a bimolecular cell.[3] F.g.a. shows that the optical-branch vibrational modes are:

	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_{1g}	E_{2g}	A_{1u}	A_{2u}	B_{1u}	B_{2u}	E_{1u}	E_{2u}
N_{opt}	7	9	7	6	13	16	5	6	9	8	16	12
ν(Si–O)	2	2	1	1	2	4	1	1	2	2	4	2

Here N_{opt} is the total vibrational representation of the unit cell ($3N$ modes) less those from the acoustic branch and ν(Si–O) is the internal-co-ordinate representation for modes chiefly involving Si–O stretching (also determined from f.g.a. tables).[4] The activities are: (Raman) A_{1g} $(xx + yy, z^2)$, E_{1g} (xz, yz), and E_{2g} $(xy, xx - yy)$; and (i.r.) A_{2u} (z) and E_{1u} (x, y). The quantity N_{opt} may be subdivided if it is assumed that $[Si_6O_{18}]^{12-}$ rings behave as essentially separate vibrational units, weakly coupled. We believe that such a distinction is invalid. In beryl, both beryllium and silicon atoms are tetrahedrally co-ordinated to oxygen. Phillips electronegativities[5] of the two elements are similar (Si 1·41, Be 1·50), but the principal quantum number of the valence shell is less for Be ($n = 2$) than for Si ($n = 3$); hence the bonding will be more strongly directional in BeO_4 than in SiO_4 groups. Indeed the highly directional nature of the bonding between beryllium and oxygen atoms is witnessed by adoption of the wurtzite structure by BeO. For these reasons it is unrealistic to subdivide N_{opt} into contributions from 'translatory' and 'rotatory' lattice modes, *etc.*; beryl is to be regarded as a lattice compound in the same sense as NaCl.

Dioptase is also hexagonal, $R\bar{3} \equiv C_{3i}^2$ with a unimolecular primitive cell, with all atoms in general positions.[6] Although this mineral is said to be hydrated, we could find no evidence of ν(OH), which is usually strong in the Raman effect, or δ(HOH) bands. Accordingly we omitted water molecules from the analysis and treated the cell contents as $6(CuSiO_3)$, thereby generating equation (1). In terms

$$N_{opt} = 15(A_g + E_g) + 14(A_u + E_u) \qquad (1)$$

of internal co-ordinates, $\Gamma(Si{-}O) = 3(A_g + E_g + A_u + E_u)$. The activities are: (Raman) A_g $(xx + yy, zz)$ and E_g $(xx - yy, xy; xz, yz)$; and (i.r.) A_u (z) and E_u (x, y).

RESULTS AND DISCUSSION

Beryl.—Fifty of the fifty-eight optically active modes of beryl were definitely observed and indications of several others obtained. This result, of itself, clearly shows that there is effectively complete vibrational coupling between the two rings, indicating that the bonding between them is strong, as was argued above.

Our i.r.-reflectance data are in good agreement with those of Gervais and Piriou[1] which appeared whilst our work was in progress, but we differ from them in our interpretation of some of the finer features of absorption spectra as computed from observed reflectance spectra. In addition, we found that A_{2u} and E_u spectra each showed a band below the limit of Gervais and Piriou's observations (see Figure 1 and Table 1).

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[1] F. Gervais and B. Piriou, *Compt. rend.*, 1972, **B274**, 252.

[2] D. M. Adams and M. M. Hargreave, *J.C.S. Dalton*, 1973, 1426.

[3] R. W. G. Wyckoff, 'Crystal Structures,' Interscience, New York, 1948, vol. 4, p. 277.

[4] D. M. Adams and D. C. Newton, 'Tables for Factor Group and Point Group Analysis,' Beckman–R.I.I.C., Croydon, 1970.

[5] J. C. Phillips, *Rev. Mod. Phys.*, 1970, **40**, 373.

[6] Ref. 3, p. 284.

In the A_{2u} spectrum five bands were clearly present below 800 cm^{-1}, showing that only one fundamental is associated with the very broad reflectance feature in the 900—1 100 cm^{-1} interval (since $6A_{2u}$ bands are predicted). Gervais and Piriou list a shoulder at 916 cm^{-1} as a fundamental, in addition to the main band at 975 cm^{-1}, but this cannot be correct as f.g.a. clearly shows that only one ν(Si–O) mode is allowed in A_{2u}. Like Gervais and Piriou, we experienced some difficulty when analysing observed reflectance data by the Kramers–Krönig method and failed to obtain acceptable results for A_{2u} species, although E_{1u} parameters (Figure 1) were readily computed. Values for A_{2u} species (Table 1) were obtained by visual estimation from observed reflectance spectra; this is quite an accurate process as a reflectance band is bounded by t.o. and l.o. mode frequencies. Also shown are estimated wavenumbers for E_{1u} species; these differ from computed values in some cases and it is not uncommon for this to happen in spectra with several bands crowded together in a relatively narrow interval.

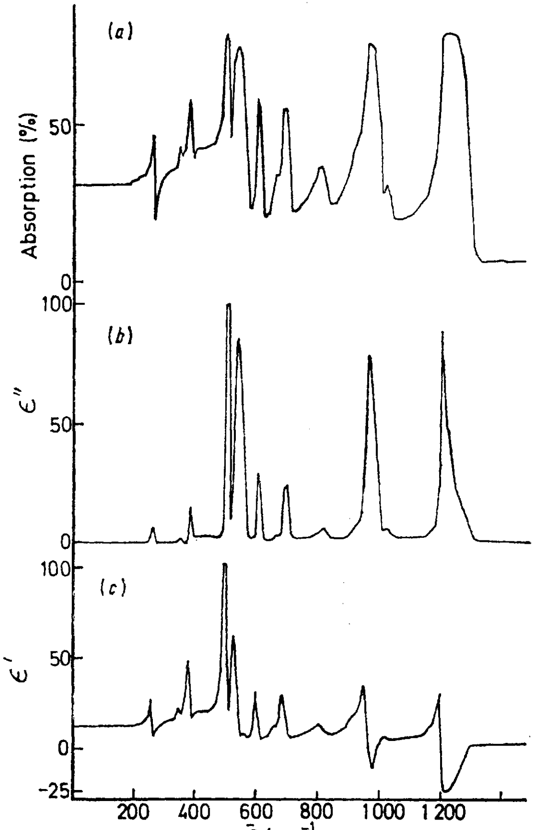

FIGURE 1 I.r.-reflectance spectrum of beryl showing results for E_{1u} species: (*a*), observed reflectance spectrum; (*c*) and (*b*), (ε') and imaginary (ε'') parts of the dielectric constant, calculated by Kramers–Krönig analysis

The tremendous breadth of the A_{2u} reflectance band at *ca.* 1 000 cm^{-1} is associated both with strong i.r. absorption and ionicity of the bonds involved, since the latter is related to l.o.–t.o. splitting. This particular ν(Si–O) mode is associated with Si–O–Be bonds, not with one of the ring oxygens Si–O–Si, since only oxygen in Wyckoff sites *m* contributes to the ν(Si–O) vector (see table 3 of ref. 4); the greater Phillips electronegativity attributed to beryllium is consistent with this observation.

TABLE 1

I.r. wavenumbers (cm^{-1}) for beryl obtained from reflectance data

A_{2u}			E_{1u}				
	t.o.		Kramers–Krönig		*a*		t.o.[b]
l.o.	*a*	*b*	l.o.	t.o.	l.o.	t.o.	
210	201		266	257	262	252	
376	361	362	352	350	350	342	350
484	419	423	391	381	387	376	382
554	532	537	510	500	510	492	488
772	734	733	552	536	564	528	517
1 100	924	916	616	600	615	596	588
			664	660	660	656	652
			710	692	706	682	674
			836	812	828	796	803
			992	962	1 002	958	955
			1 044	1 020	1 032	1 014	1 016
			1 288	1 198	1 292	1 200	1 196

t.o. and l.o. = Transverse and longitudinal optics.

[a] This work; estimated values (see text). [b] Ref. 1.

Twelve of the predicted sixteen E_{1u} bands were clearly present; Gervais and Piriou gave two further bands at 519 and 979 cm^{-1} because it was necessary to add these oscillators to obtain a good fit with the observed reflectance using the harmonic-oscillator model. Our computed ε'' spectra do not exclude these as possibilities, but there are several other weak features which might also be identified with missing bands. Four ν(Si–O) bands are expected in E_{1u}: bands at 955, 1 016, and 1 196 cm^{-1} are certainly three of them, but it is not clear whether that at 803 cm^{-1} is the fourth; if not, the weak 979 cm^{-1} oscillator may be it. However, all the A_{2u} and twelve of the sixteen E_{1u} modes have been definitely located.

The Raman spectra showed good extinctions between spectra determined for the various tensor components (Table 2). A clear gap of *ca.* 150 cm^{-1} separated the ν(Si–O) modes from others; all the eight predicted modes were found. The chief ambiguities arose in the region below 300 cm^{-1} where several rather broad features were found (see Figure 2). For A_{1g} species, six of the seven expected bands were above 300 cm^{-1} and of normal breadth and appearance. A further broad band was centred at 214 cm^{-1}; its appearance was unchanged on cooling to liquid-nitrogen temperature, and even at ambient temperature showed signs of structure. In fact, all the A_{1g} modes derive entirely from motions of the $[Si_6O_{18}]^{12-}$ ring, since Al and Be are in Wyckoff sites which do not contribute to the A_{1g} representation. Therefore, we cannot account for this breadth by postulating isomorphous replacement in the mineral. Clearly, some aluminium atoms may have been substituted for silicon in the ring, but we consider that, if this had happened to an extent detectable by Raman spectroscopy, more than one mode should have shown the effect. If we had treated this material as containing $[Si_6O_{18}]^{12-}$ ions with relatively weak bonds to neighbours, we should have found that the lowest of the seven A_{1g} modes corresponds to restricted rotation of the rings about the z axis. (The representation for the six degrees of rotation of the rings is $A_{1g} + A_{2g} + 2E_{1g}$.) Although the interionic bonding is not weak, this low-frequency mode nevertheless involves rotational-type movements (more correctly described as complex deformations). The 214 cm^{-1} band is also unique in being the only A_{1g} mode to appear in the (zz) but not in (xx) and (yy) spectra. Although we are by no means convinced that abnormal breadth of a low-frequency band is associated with quasi-rotatory motion, we note that the only other band showing such behaviour is in E_{1g} (at *ca.* 188 cm^{-1}): this species, but not E_{2g}, also has rotatory modes allowed on the 'weak-bonding' model.

TABLE 2
Raman wavenumbers (cm^{-1}) and intensities (arbitrary scale) for single-crystal beryl

		$x(zz)y$	$y(xx)z$	$y(xy)z$	$y(zx)z$
145	E_{1g}				19
146	E_{2g}		6	6	
187	E_{2g}		9	7	
188br	E_{1g}				8
214br	A_g	15			
254	E_{1g}				9
291	E_{2g}		18	8	
297	E_{1g}				7
318	E_{2g}			13	
324	A_g	166	83		
383	E_{1g}				7
396	A_g	166	160		
397	E_{2g}			9	
424	E_{2g}		43	32	
444	E_{2g}		33	29	
450	E_{1g}				35
529	E_{1g}				60
565	E_{2g}		5	6	
583	E_{2g}		22	20	
626	A_g	25	6		
683	E_{1g}				11
685	E_{2g}			21	
686	A_g	525	470		
770	E_{1g}				12
772	E_{2g}		19	14	
914	E_{2g}		8	8	
918	E_{1g}				14
1 005	E_{2g}		20	17	
1 012	E_{1g}				86
1 068	A_g	625	63	3	6
ca. 1 125sh	A_g	8			
ca. 1 225sh	E_{2g}		6	8	
1 243	E_{2g}		33	30	

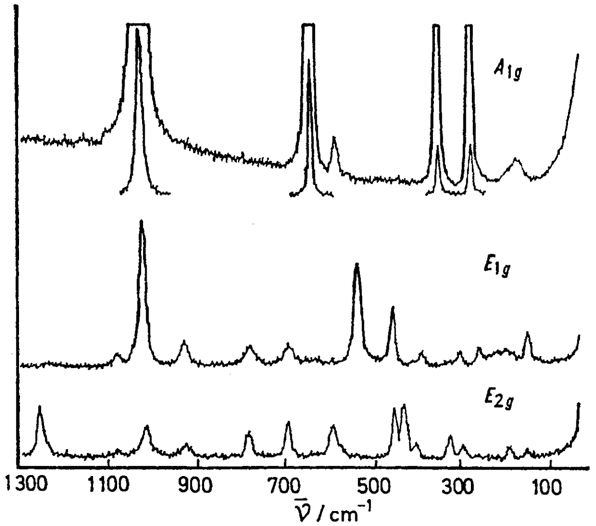

FIGURE 2 Raman spectrum of beryl: spectral slit width 6 cm^{-1}; 488·0 nm excitation, *ca.* 150 mW at sample. Inset for A_g shows spectrum at 2 cm^{-1} spectral slit width

In the region below 800 cm^{-1}, 9/11 and 11/12 of the E_{1g} and E_{2g} modes respectively were located, including a few accidental coincidences. For example, extinctions between the spectra were good, as can be seen from the non-appearance of a strong band from spectra in other orientations. Hence, when two or more orientations show a feature at the same frequency, it must be concluded that it is from different symmetry species and not a residual.

Dioptase.—The crystal of dioptase available to us, though of fairly good optical quality, was too small to permit i.r.-reflectance spectra of good quality to be obtained suitable for analysis by either of the usual methods. Nevertheless, t.o. wavenumbers were estimated from positions of reflectance maxima and are listed in Table 3. Inevitably some of the weaker bands have been missed, but it is gratifying that ten of the fourteen predicted E_u bands should have been found under these conditions.

TABLE 3
I.r. wavenumbers (cm^{-1}) for t.o. modes of dioptase estimated visually from reflectance spectra. The factor group is C_{3i}

A_u	E_u
78	140
256	372
344	412
774	440
876	500
978	564
	ca. 642
	ca. 760
	932
	986

The Raman selection rules show that E_g modes appear in all spectra other than (zz). In comparison with beryl, the Raman spectra were very complex, showing clearly that it is the factor-group rules which operate, and not an approximation to a slightly perturbed D_{6h} ring. However, bonding between the ring oxygen atoms and copper is less strong than with beryllium and we note that the highest ν(Si–O) in dioptase is at 1 008 cm^{-1}; *cf.* 1 243 cm^{-1} in beryl, but 1 020 cm^{-1} in $(Me_2SiO)_3$ which has the same ring type.[7] In further contrast to beryl, which has its lowest Raman mode at 145 cm^{-1} and nothing in the i.r. spectrum below 250 cm^{-1}, dioptase showed activity below 100 cm^{-1} in both spectra, indicative of weaker ring–neighbour bonding. Since fifteen modes are predicted for each Raman-active species (A_g and E_g) some accidental coincidences are to be expected. Extinctions were not perfect and some doubt exists for several bands as to whether or not A_g

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[7] D. M. Adams and W. S. Fernando, *J.C.S. Dalton*, 1973, 410.

and E_g modes are accidentally degenerate. Twenty-five Raman bands were observed, in itself evidence that the full factor-group rules apply. Counting bands for each species shows that at least fifteen are present, raising the possibility that the true total may be above that predicted above. This may indicate that water molecules contribute observable translatory and rotatory modes ($3A_g + 3A_u + 3E_g + 3E_u$ are expected) to the low-frequency spectrum whilst not showing ν(OH) modes.

Further discussion of the dioptase spectra is unprofitable without new evidence from larger and more perfect crystals. However, the main conclusions are clear: spectra must be considered on the basis of factor-group rules, not those of a slightly perturbed beryl-type ring; and the bonding between rings and counter-ions in beryl and dioptase is very different.

TABLE 4

Raman wavenumbers (cm^{-1}) and relative intensities (arbitrary units) for single-crystal dioptase

	$x(zz)y$	$x(zx)y$
73	>100	24
98	12	37
116	4	15
132	28	20
160	6	16
178	10	6
196		6
221		23
226	26	
241		10
267	26	12
291	33	
295		24
324	7	10
356	>100	24
398	52	14
428	34	10
454		10
488	7	
524	6	11
660	30	9
744		7
913		3
956	7	
1 008	6	8

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