Solid-state Vibrational Spectroscopy. Part IV.[1] A Vibrational and Differential Scanning Calorimetry Study of the Polymorphism of Sodium and Potassium Sulphates

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The polymorphism of sodium and potassium sulphates has been studied using differential scanning calorimetry (d.s.c.) and vibrational spectroscopy. For $Na_2[SO_4]$ the d.s.c. study has yielded enthalpy changes for the various phase transitions. The polymorphs have distinct Raman spectra whereas the i.r. spectra do not show such distinct differences. The phase-transition temperature of $K_2[SO_4]$ is outside the range of the d.s.c. instrument, but the vibrational spectra indicate that $K_2[SO_4]$, unlike $Na_2[SO_4]$, does not exist in a metastable phase on cooling below the transition temperature.

SODIUM SULPHATE.—The polymorphism of sodium sulphate was extensively studied by Kracek[2] who postulated the existence of five distinct polymorphs. The most recent study[3] suggests the transitions (1) and (2). Phase (I) is stable up to the m.p., but, on cooling, it gives the metastable polymorph (III).

$$\text{(V)} \xrightarrow{458\ \text{K}} \text{(IV)},\ \Delta H = 0.3\ \text{kJ mol}^{-1} \qquad (1)$$

$$\text{(IV)} \xrightarrow{514\ \text{K}} \text{(I)},\ \Delta H = 10.9\ \text{kJ mol}^{-1} \qquad (2)$$

Phase (V) is orthorhombic with space group D_{2h}^{24} (*Fddd*) containing eight molecules in the crystallographic unit cell and two molecules in the Bravais unit cell.[4] The correlation between the T_d point group of the $[SO_4]^{2-}$ anion, the D_2 site symmetry, and the D_{2h} space group is given in Table 1. The free sulphate anion gives rise to four Raman and two i.r. bands, with two coincidences, site-group splitting gives rise to nine Raman and six i.r. bands with six coinci-

TABLE 1

Correlations for the sulphate salts

(*a*) $Na_2[SO_4]$ (V)

T_d	D_2	D_{2h}
a_1 (R)	$\rightarrow a$(R)	$a \rightarrow a_g$ (R) + a_u (I)
e(R)	$\rightarrow 2a$(R)	$b_1 \rightarrow b_{1g}$(R) + b_{1u} (I.r.)
$2f_2$ (I.r., R)	$\rightarrow 2[b_1$ (I.r., R) + b_2 (I.r., R) + b_3 (I.r., R)]	$b_2 \rightarrow b_{2g}$(R) + b_{2u} (I.r.)
		$b_3 \rightarrow b_{3g}$ (R) + b_{3u} (I.r.)

(*b*) $Na_2[SO_4]$ (III)

T_d	C_{2v}	D_{2h} [correlating about C_2 (*y*)]
a_1 (R)	$\rightarrow a_1$ (I.r., R)	$a_1 \rightarrow a_g$ (R) + b_{2u} (I.r.)
e(R)	$\rightarrow a_1$ (I.r., R) + a_2 (R)	$a_2 \rightarrow b_{2g}$ (R) + a_u (I)
$2f_2$ (I.r., R)	$\rightarrow 2[a_1$(I.r., R) + b_1 (I.r., R) + b_2 (I.r., R)]	$b_1 \rightarrow b_{3g}$ (R) + b_{1u} (I.r.)
		$b_2 \rightarrow b_{1g}$ (R) + b_{3u} (I.r.)

(*c*) $K_2[SO_4]$(II)

T_d	C_s	D_{2h} (correlating about σ_{zx})
a_1 (R)	$\rightarrow a'$ (I.r., R)	$a' \rightarrow a_g$ (R) + b_{2g} (R) + b_{1u} (I.r.) + b_{3u} (I.r.)
e(R)	$\rightarrow a'$ (I.r., R) + a'' (I.r., R)	
$2f_2$ (I.r., R)	$\rightarrow 4a'$ (I.r., R) + $2a''$ (I.r., R)	$a'' \rightarrow b_{1g}$ (R) + b_{3g} (R) + a_u (I) + b_{2u} (I.r.)

I = Inactive.

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[1] Part III, J. E. D. Davies, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1531.

[2] F. C. Kracek, *J. Phys. Chem.*, 1929, **33**, 1281.

[3] G. E. Brodale and W. F. Giauque, *J. Phys. Chem.*, 1972, **76**, 737.

[4] A. G. Nord, *Acta Chem. Scand.*, 1973, **27**, 814.

dences, whilst factor-group splitting also gives rise to nine Raman and six i.r. bands but with no coincidences.

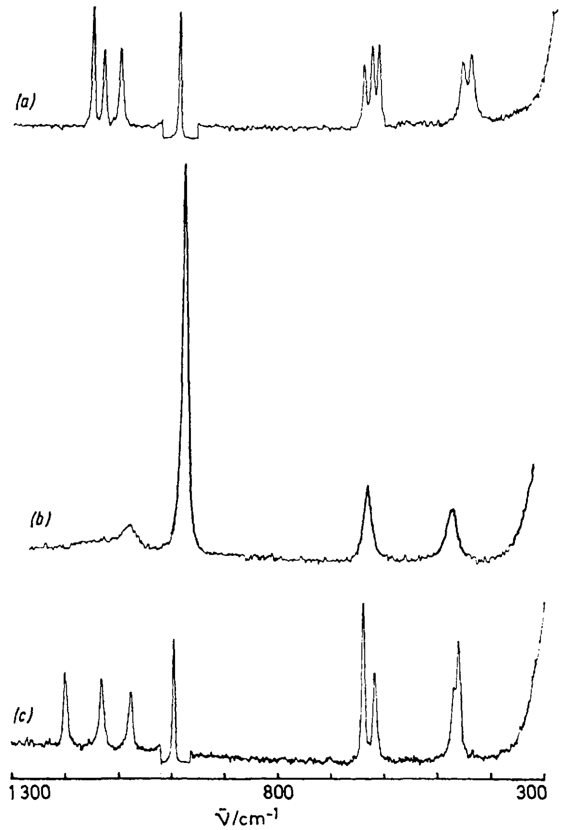

FIGURE 1 Raman spectra of (*a*) $Na_2[SO_4]$(V) at 296 K, (*b*) $Na_2[SO_4]$(I) at 564 K, (*c*) $Na_2[SO_4]$(III) at 301 K. In (*a*) and (*c*) the band at 990 cm^{-1} was recorded using one tenth the sensitivity used for the remaining part of the spectra

Phase (III) is regarded as being isomorphous with $Na_2[CrO_4]$ with site symmetry C_{2v}, and space group D_{2h}^{17} (*Cmcm*), containing two molecules per Bravais unit cell.[5] The relevant correlation is given in Table 1. Both site- and factor-group splitting give rise to nine Raman and eight i.r. bands, but there are eight coincidences for site-group and no coincidences for factor-group splitting. The crystal structure of phase (I) has not been established definitely. It is thought [6] to be isomorphous with either $LiK[SO_4]$ (C_6^6) or $NaK[SO_4]$ (D_{3d}^3).

The Raman spectrum of phase (V) at 296 K is shown in Figure 1(*a*) and the low-temperature i.r. and Raman data are in Table 2. There was no significant difference between the room- and low-temperature data indicating that there was no phase change in the 68—296 K region. The i.r. and Raman data for ν_4 indicate that factor-group splitting is operative in phase (V).

When heated in the high-temperature Raman cell the spectrum of phase (V) was observed at 420 and 485 K. According to Brodale and Giauque [3] the latter temperature is in the region of stability of phase (IV), implying that either the polymorphs (V) and (IV) have identical Raman spectra or that the transition represented by (1) does not occur. The differential scanning calorimetry (d.s.c.) study also did not reveal a peak at 458 K corresponding to this transition, although the peak would in any case be of low intensity due to the small ΔH value reported. Combination of the Raman and the d.s.c. data, however, throws some doubt on the existence of the $Na_2[SO_4]$(IV) phase.

The transition (V) $\longrightarrow$ (I) gave rise to a very broad, ill-defined, endothermic d.s.c. peak, ranging from 493 to 553 K, maximized at 526 K, and giving a ΔH value of 10.8 kJ mol^{-1}. On heating the sample of (V) to 564 K, a new Raman spectrum due to phase (I) was obtained [Figure 1(*b*)]. Cooling of phase (I) in the d.s.c. instrument gave an exothermic peak corresponding to the transition (I) $\longrightarrow$ (III) and a ΔH value of 6.7 kJ mol^{-1}. The Raman spectrum of phase (III) at 301 K is shown in Figure 1(*c*). A similar spectrum was recorded at 68 K (Table 2), illustrating the stability of this metastable phase. Comparison of the i.r. and Raman data for ν_1 and ν_4 indicates that factor-group splitting is operative in phase (III). The latter is isomorphous with $Na_2[CrO_4]$, and the Raman spectra of these two salts have some

TABLE 2

Vibrational spectra (cm^{-1}) of the polymorphs of sodium and potassium sulphates*

	$[SO_4]^{2-}$ (aq) Raman	$Na_2[SO_4]$(V)		$Na_2[SO_4]$(I) Raman (564 K)	$Na_2[SO_4]$(III)		$K_2[SO_4]$(II)	
		Raman (68 K)	I.r. (113 K)		Raman (68 K)	I.r. (113 K)	Raman (68 K)	I.r. (118 K)
		450 (0.6)			460 (0.9)		450 (0.4)	
$\nu_2(e)$	450 (1.1)			460 (1.3)				
		468 (0.5)			470 (0.6)		458 (1.3)	
		621 (0.6)	612vs		615 (0.7)	610vs	618 (sh)	614vs
$\nu_4(f_2)$	620 (0.4)	633 (0.6)	636vs	630 (1.9)		619vs	622 (1.0)	618vs
		650 (0.5)			640 (1.2)	634vs	630 (0.6)	
$\nu_1(a_1)[SO_3{}^{17}O]^{2-}$		977vvw			978vvw		973vvw	
$\nu_1(a_1)[SO_4]^{2-}$	982 (10.0)	993 (10.0)		995 (10.0)	997 (10.0)	996w	987 (10.0)	986vw
		1 102 (0.7)			1 077 (0.4)		1 088 (0.1)	
$\nu_3(f_2)$	1 110 (0.4)	1 134 (0.6)	*ca.* 1 110	1 100 (0.5)	1 137 (0.5)	*ca.* 1 110	1 096 (0.3)	*ca.* 1 110
		1 154 (1.0)	vs, b		1 205 (0.5)	vs, b	1 109 (0.5)	vs, b
							1 113 (0.5)	
							1 150 (0.7)	

* The figures in parentheses indicate the relative peak heights of the bands uncorrected for photomultiplier response.

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[5] H. Fischmeister, *Acta Cryst.*, 1954, **7**, 776.

[6] H. F. Fischmeister, *Monatsch.*, 1962, **93**, 420.

common features such as the splitting of ν_4 into two components [7,8] rather than into the three expected.

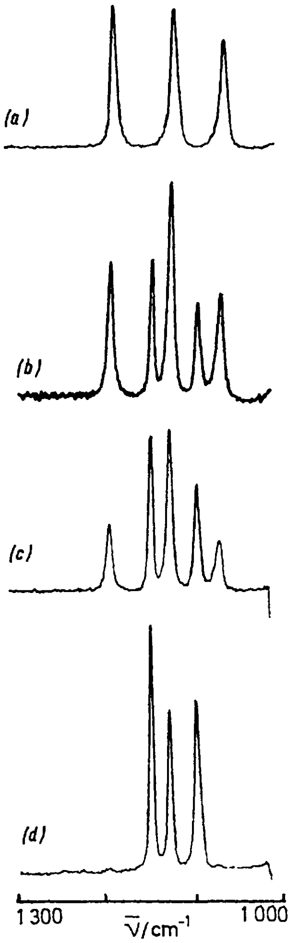

FIGURE 2 Raman spectra of $Na_2[SO_4]$(III): (*a*) freshly prepared; (*b*) 9 weeks after preparation; (*c*) 19 weeks after preparation; (*d*) 11 months after preparation

Further heating–cooling cycles of phase (III) in the d.s.c. instrument and in the Raman cell showed that transitions (III) → (I) and (I) → (III) were being observed, with the d.s.c. peaks showing the hysteresis which had been reported in a previous differential thermal analysis (d.t.a.) study.[9] Similar spectral and thermal changes were observed starting with a sample of freshly prepared phase (III).

The transition (III) → (V). It has been noted previously [3] that metastable phase (III) is in fact very stable if kept in a dry atmosphere, but reverts to the more stable phase (V) in the presence of moisture.

A freshly prepared sample of phase (III) was divided into two portions, one of which was stored in dry air whilst the other was stored in undried air. Raman spectra (1 000—1 300 cm^{-3}) of the portion stored in undried air recorded over a period of time are shown in Figure 2. The gradual conversion of phase (III) into (V), complete after *ca.* 11 months, is illustrated. During this period the sample of phase (III) stored in dry air showed no sign of conversion into phase (V), and indeed there was still no sign of conversion 20 months after preparation.

The pressure-induced transition (III) → (V). During the preparation of discs of phase (III) for mounting in the Raman cryostat it was noted that there was some conversion into phase (V). A quantitative study of this pressure-induced transition was undertaken by using 300 mg of sample and subjecting it to different pressures for 1 min. The die was evacuated during the preparation to eliminate interfering effects which might be caused by the presence of any moisture. Raman spectra (1 000—1 300 cm^{-1}) of the discs are shown in Figure 3 where there is a correlation between the applied pressure and the degree of conversion into phase (V).

Potassium Sulphate.—Potassium sulphate undergoes a phase transition at 858 K from the polymorph (II) to (I).[10] Phase (II) is isomorphous with $K_2[CrO_4]$, being orthorhombic with space group D_{2h}^{16} (*Pnam*) and four molecules in the unit cell.[11] The correlations are shown

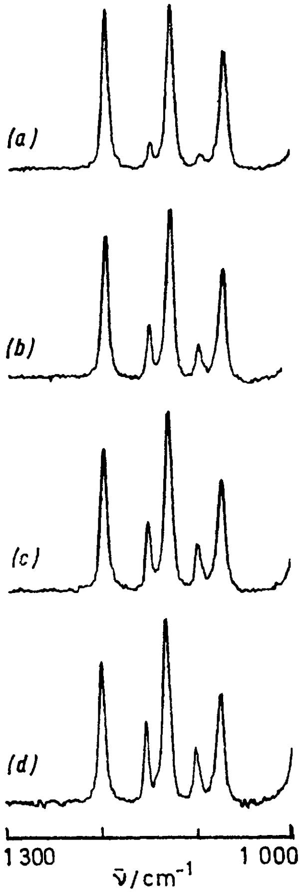

FIGURE 3 Raman spectra obtained from discs prepared by subjecting phase (III) (300 mg) to pressures of (*a*) 5 000, (*b*) 10 000, (*c*) 15 000, and (*d*) 20 000 N m^{-2} for 1 min

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[7] J. E. D. Davies and D. A. Long, *J. Chem. Soc.* (*A*), 1971, 1275.

[8] R. L. Carter and C. E. Bricker, *Spectrochim. Acta*, 1974, **A30**, 1793.

[9] Q. R. Goyal, V. V. Deshpande, and M. D. Karkhanavala, *Indian J. Chem.*, 1971, **9**, 1006.

[10] R. Moreau, *Bull. Soc. roy. Sci. Liège*, 1963, **32**, 252.

[11] J. A. McGinnety, *Acta Cryst.*, 1972, **B28**, 2845.

in Table 1 and the observed i.r. and Raman spectra are in Table 2. The observed Raman spectrum of the powder bears some similarity to that of the isomorphous compound $K_2[CrO_4]$ in that $\nu_3(f_2)$ is split into five components in $K_2[SO_4]$ and into six components [8] in $K_2[CrO_4]$. The powder Raman spectrum is also in good agreement with recently reported single-crystal Raman data.[12]

The (II) $\longrightarrow$ (I) transition temperature of 858 K is outside the range of both the d.s.c. instrument * and of the high-temperature Raman cell. A sample of phase (II) was, however, heated to 973 K and allowed to cool to room temperature. The Raman spectrum of the product was identical to that of phase (II), indicating that, unlike $Na_2[SO_4]$(V), $K_2[SO_4]$(II) does not cool to a metastable phase. The room-temperature and 68 K Raman spectra of phase (II) were also identical indicating no phase change between these temperatures.

EXPERIMENTAL

AnalaR samples of $Na_2[SO_4]$(V) and $K_2[SO_4]$(II) were used without further purification; $Na_2[SO_4]$(III) was prepared by heating $Na_2[SO_4]$(V) at 673 K for 24 h.

D.s.c. traces in the range 173—773 K were recorded using a Perkin-Elmer D.S.C.-1B instrument, and a heating rate of 8° min^{-1}. The enthalpy changes were calculated using indium as standard. I.r. spectra of Nujol mulls in the range 4 000—200 cm^{-1} were recorded on a Perkin-Elmer 225 spectrometer which was calibrated using polystyrene film. The low-temperature spectra were obtained using a Beckman-RIIC variable-temperature unit. Raman spectra were excited using a Coherent Radiation Laboratories model 52 argon–krypton laser and were recorded on a Cary 81 spectrometer. Room-temperature spectra of powders were recorded using the standard 180° sampling arrangement, but the 90° arrangement was used when recording the high- and low-temperature spectra. The Kr^+ 520.8 nm line was used for excitation, giving *ca.* 30 mW power at the sample for the 180° arrangement and *ca.* 150 mW power at the sample for the 90° arrangement. The spectrometer was calibrated using krypton emission lines and a slit width of 3 cm^{-1} was used for all spectra. The low-temperature spectra were recorded using an Oxford Instruments CF 104 continuous-flow cryostat. The use of liquid nitrogen as a coolant gave a base temperature of 68 K. The high-temperature cell and controller were built in the department. It was manufactured from a brass block and wound with a heating coil and gave a maximum temperature of 843 K.

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* Potassium sulphate gave an endothermic peak at 858 K when examined on the Perkin-Elmer D.S.C.-2 instrument.

[12] M. Debeau, *Rev. Phys. Appl.*, 1972, **7**, 49; S. Montero, R. Schmoelz, and S. Haussuehl, *J. Raman Spectroscopy*, 1974, **2**, 101; F. Meserole, J. C. Decius, and R. E. Carlson, *Spectrochim. Acta*, 1974, **A30**, 2179.