An effect similar to that observed in AgI at room temperature was noticed by Hoshino (1952) in powder photographs at 430°C of the wurtzite phase of CuBr. An analogous effect occurred for the zincblende phase of the same powder observed at room temperature. Interpretation of both effects as anharmonic thermal vibration would again appear to provide a better approximation to the true situation. This was, in fact, recognized by Miyake & Hoshino (1958) in a review of the work. Further experimental study of these halides would evidently provide valuable quantitative results for the cubic anharmonic parameters introduced in the early part of this paper.

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References

ADRIAN, H. W. W. & FEIL, D. (1969). *Acta Cryst.* A**25**, 438–444.
BARNEA, Z. (1973). Ph. D. Thesis, Univ. of Melbourne.
BERLINCOURT, D., JAFFE, H. & SHIOZAWA, L. R. (1963). *Phys. Rev.* **129**, 1009–1017.
BURLEY, G. (1963). *J. Chem. Phys.* **38**, 2807–2812.
COOPER, M. J., ROUSE, K. D. & FUESS, H. (1973). *Acta Cryst.* A**29**, 49–56.
DAWSON, B. (1967). *Proc. Roy. Soc.* A**298**, 255–263.
DAWSON, B. & WILLIS, B. T. M. (1967). *Proc. Roy. Soc.* A**298**, 307–315.
GROUT, P. J. & MARCH, N. H. (1974). *Phys. Lett.* **47**A, 288–290.
HEILAND, G. & IBACH, H. (1966). *Sol. State Commun.* **4**, 353–356.
HELMHOLZ, L. (1935). *J. Chem. Phys.* **3**, 740–747.
HOSHINO, S. (1952). *J. Phys. Soc. Japan*, **7**, 560–571.
JEFFREY, G. A., PARRY, G. S. & MOZZI, R. L. (1956). *J. Chem. Phys.* **25**, 1024–1031.
KEFFER, F. & PORTIS, A. M. (1957). *J. Chem. Phys.* **27**, 675–682.
LAWAETZ, P. (1972). *Phys. Rev.* B**5**, 4039–4045.
MIYAKE, S. & HOSHINO, S. (1958). *Rev. Mod. Phys.* **30**, 172–174.
NYE, J. F. (1957). *Physical Properties of Crystals*, p. 187. Oxford: Clarendon Press.
PHILLIPS, J. C. (1970). *Rev. Mod. Phys.* **42**, 317–356.
PRYOR, A. W. & SABINE, T. M. (1964). *J. Nucl. Mater.* **14**, 275–281.
SABINE, T. M. & HOGG, S. (1969). *Acta Cryst.* B**25**, 2254–2256.
SMITH, D. K., NEWKIRK, H. W. & KAHN, J. S. (1964). *J. Electrochem. Soc.* **111**, 78–87.
WILLIS, B. T. M. (1969). *Acta Cryst.* A**25**, 277–300.

Acta Cryst.(1975). A**31**, 207

Thermoelastic Properties of Potassium Hydrogen Sulphate

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The room-temperature elastic moduli, their temperature derivatives and the thermal expansion of $KHSO_4$ have been measured. Both the elastic and the thermal properties exhibit a quasi-hexagonal symmetry, the crystalline *a* axis being the unique axis. On the other hand, the Grüneisen tensor is essentially isotropic. A qualitative correlation of these phenomena with the crystal structure is made.

Introduction

The family of the hydrogen sulphate salts form an interesting group of materials, as the binding in the crystal is characterized by the presence of strong hydrogen bonds. These bonds are also responsible for the ferroelectric phase transitions found in ammonium and rubidium hydrogen sulphates, (Pepinsky, Vedam, Hoshino & Okaya, 1958; Pepinsky & Vedam, 1960). Although the ferroelectric phase transition in the latter materials has been investigated extensively, no elastic data are available for any material in the above group. Thus, an investigation of the thermoelastic properties of potassium hydrogen sulphate, $KHSO_4$, as the first of the HSO_4 group, was undertaken. In addition to the existence of hydrogen bonds (Loopstra & MacGillavry, 1958), the material is known to have several phase transitions (Bridgman, 1916/1917). It should therefore be of interest to measure its thermoelastic properties, to try to correlate the latter with the direction and strength of the existing hydrogen bonds, and to see whether any indication of the occurrence of

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the phase transitions can be deduced from the behaviour of its elastic properties.

With this in mind, an investigation of the thermoelastic properties of $KHSO_4$ was undertaken. The present work reports measurements of the room-temperature elastic moduli, their temperature derivatives and the thermal expansion of single-crystal $KHSO_4$.

Measurements

Large single crystals of $KHSO_4$ of optical quality were grown from aqueous sulphuric acid solutions by slow evaporation. The crystals were oriented by their natural faces, and rectangular-shaped specimens, with their faces in specified crystalline directions, were cut out with a string saw. Final polishing of the faces to a parallelism of about 20″ was done by hand lapping, with 3μm corundum polishing powder.

$KHSO_4$ is orthorhombic, point symmetry group *mmm*. A set of Cartesian axes a_1, a_2 and a_3 was fixed in the crystal, parallel to its crystalline axis. All directions are referred to the above Cartesian axis. The crystal has nine independent elastic moduli, c_{11}, c_{22}, c_{33}, c_{12}, c_{13}, c_{23}, c_{44}, c_{55} and c_{66}, the Voigt notation being used throughout. They were determined by measuring the sound velocities in various crystalline directions, by the improved Schaefer–Bergmann method (Haussühl, 1956) (diffraction of light at standing ultrasonic waves at frequencies of about 15 MHz). The results were verified by measuring the eigenfrequencies of thick plates in the same crystalline directions, and also by some additional pulse echo measurements, for directions in which no light diffraction could be obtained. From the measured sound velocities the elastic moduli were computed.

The temperature derivatives of the moduli were determined from the variation of the eigenfrequencies with temperature, over the range 20 to 0 °C. The thermal expansion was determined from the length changes in the range 20 to 80 °C, measured with a variable-inductance transformer dilatometer. The density of the material was measured by hydrostatic weighing.

Results

The measured sound velocities and the temperature derivatives of the eigenfrequencies for the various crystalline directions are shown in Table 1. The values of the thermal expansion, α_{ii}, and density, are presented in Table 2. From these experimental data the elastic stiffness, c_{ij}, and compliance, s_{ij}, moduli, as well as the temperature derivatives, $T_{ij}(\partial \ln c_{ij}/\partial T)$, and the relative errors of the former were deduced, and are shown in Table 3.

Table 1. *Measured values of sound velocities and temperatures derivatives of eigenfrequencies*

No.	Direction	Type of wave	Sound velocity (10^5 cm s^{-1})	Temperature derivative of eigenfrequency [10^{-4} (°C)$^{-1}$]
1	[100]	Longitudinal	4·743	−4·4
2	[010]	Longitudinal	3·639	−3·0
3	[001]	Longitudinal	3·682	−4·1
4	[110]	q.l.*	4·174	−3·9
5	[110]	q.s.†	2·314	−4·6
6	[101]	q.l.	4·307	−3·8
7	[101]	q.s.	2·285	−6·5
8	[011]	q.l.	3·935	−3·6
9	[011]	q.s.	1·838	−3·6

* q.l. quasi-longitudinal.
† q.s. quasi-shear.

Table 2. *Thermal expansion and density*

α_{ii} are in 10^{-6} (°C)$^{-1}$, density in g cm^{-3}.

α_{11}	α_{22}	α_{33}	Density
5·6	59	68	2·3144

Table 3. *Elastic stiffness and compliance moduli, and temperature derivatives of the former*

ij	c_{ij} (10^{11} dyn cm^{-2})	s_{ij} (10^{-12} cm^2 dyn^{-1})	T_{ij} [10^{-3}(°C)$^{-1}$]
11	5·698 ± 0·2 %	2·204	−1·00
22	3·060 ± 0·3 %	4·538	−0·60
33	3·138 ± 0·3 %	4·555	−0·81
12	1·558 ± 3 %	−0·687	−0·36
13	1·715 ± 2 %	−0·869	−0·16
23	1·530 ± 2 %	−1·837	−0·67
44	1·271 ± 1 %	7·869	−0·78
55	1·097 ± 2 %	9·118	−0·96
66	0·899 ± 3 %	11·14	−1·22

As the c_{ij} are obtained from the solution of a quadratic equation, two values, one positive and one negative, are obtained for each of the constants c_{12}, c_{13} and c_{23}. But only the selection of all three positive values simultaneously, renders the value of the 6×6 determinant of the elastic moduli positive, any other combination resulting in a negative value. Thus, an unambiguous choice can be made, which is that shown in Table 3.

The errors in the c_{ij} were computed by error propagation, assuming an inaccuracy of 0·1 % in the measurements of the sound velocities.

Discussion

Because of the complexity of the crystalline unit-cell structure, no detailed lattice dynamical calculation of the elastic moduli will be attempted. On the other hand, some qualitative correlation between the crystal structure of $KHSO_4$, and the form of the elastic moduli and thermal expansion tensors will be made.

On inspection of Table 3 it is immediately evident that as far as the elastic properties are concerned, $KHSO_4$ looks as if its structure is hexagonal, the *a* axis being the hexagonal sixfold axis and the *bc* plane the basal plane. This uniqueness of the *a* axis must be intimately connected with the direction of the hydrogen bonds in the crystal, which form chains running parallel to the *a* axis (Loopstra & MacGillavry, 1958). The crystal will thus exhibit its highest elastic stiffness in the **a** direction, which is also borne out by the experimental results for the elastic moduli. This uniqueness of the *a* axis is also demonstrated by the thermal expansion, which is smaller by an order of magnitude in the **a** direction, compared with the **b** and **c** directions, and by the deviations from the Cauchy relations. The latter form a second-rank tensor, defined by (Haussühl, 1967)

$$c_{iijk}-c_{ijik}=(2\delta_{mn}-1)g_{mn} \qquad (1)$$

with $m\neq i,j$; $n\neq i,k$, and $m,n,i,j,k=1,2,3$, δ_{mn} being the Kronecker symbol. The tensor components g_{ii} are shown in Table 4, and as can be seen, g_{11} is less than half of g_{22} or g_{33}.

Table 4. *Deviations from the Cauchy relations*

Units are 10^{11} dyn cm^{-2}.

g_{11}	g_{22}	g_{33}
0·259	0·618	0·660

On the other hand, the above uniqueness of the *a* axis is not shown by the Grüneisen tensor, whose components are shown in Table 5. The latter were computed from the thermal expansion and the room-temperature specific heat of 33·2 cal mol^{-1} deg^{-1} (Kopp, 1864/1865). This is not surprising, as even for materials with a very high anisotropy in their elastic and thermal properties, the Grüneisen tensor tends to be considerably less anisotropic (Küppers, 1974).

Table 5. *Components of the Grüneisen tensor*

γ_{11}	γ_{22}	γ_{33}
1·01	1·24	1·33

A comparison between the average elastic stiffness of two substances, I and II, can be made by computing the ratio (Haussühl, 1963)

$$\frac{Q(\mathrm{I})}{Q(\mathrm{II})}=\frac{V_{\mathrm{mole}}(\mathrm{I})^{4/3}/K(\mathrm{I})}{V_{\mathrm{mole}}(\mathrm{II})^{4/3}/K(\mathrm{II})}\,.$$

Here, V_{mole} is the volume per molecule, and K the compressibility. The above ratio should be close to 1 for materials with predominantly ionic binding and similar chemical composition. Normalizing $Q(KHSO_4)$ to 1, Q (K_2SO_4) becomes 1·65. This is in agreement with results found in other groups of materials (Gerlich & Haussühl, 1974), where a replacement of the proton by a monovalent cation increases the value of Q.

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References

BRIDGMAN, P. W. (1916/1917). *Proc. Amer. Acad. Arts Sci.* **52**, 91.

GERLICH, D. & HAUSSÜHL, S. (1974). Submitted for publication.

HAUSSÜHL, S. (1956). *Naturwissenschaften*, **43**, 294–395.

HAUSSÜHL, S. (1963). *Phys. Stat. Sol.* **3**, 1072–1076.

HAUSSÜHL, S. (1967). *Phys. kond. Mater.* **6**, 181–192.

KOPP, H. (1864/1865). *Liebigs Ann. Suppl.* **3**, 296.

KÜPPERS, H. (1974). Submitted for publication.

LOOPSTRA, L. H. & MACGILLAVRY, C. H. (1958). *Acta Cryst.* **11**, 349–354.

PEPINSKY, R. & VEDAM, K. (1960). *Phys. Rev.* **117**, 1502–1503.

PEPINSKY, R., VEDAM, K., OKAYA, Y. & HOSHINO, S. (1958). *Phys. Rev.* **111**, 1508–1510.