# The Phase Transition of Potassium Sulfate

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The discontinuous phase transition of $K_2SO_4$ is described by a semi-empirical model that uses the elastic stiffnesses $c_{ii}$ and the changes in volume and entropy associated with the order-disorder transition. Consideration of the elastic anomaly (existence of soft, damped *longitudinal* acoustic phonons) in $K_2SO_4$ removes the disagreement between transition enthalpies $\Delta H_{tr}$ measured calorimetrically and $\Delta H_{tr}$ derived from the p-T phase diagram via the Clausius-Clapeyron equation. The model used requires the knowledge of the $c_{ii}$ ($i=1, 2, 3$) which in many cases is not available in the literature. It is demonstrated that these values can be calculated with sufficient accuracy from the anisotropic displacement (Debye-Waller) factors which are routinely determined in crystal structure analyses and which, therefore, are available for many substances. There is fair agreement between the calculated strain energy and $\Delta H_{tr}$ also for $K_2SeO_4$. In the case of $K_2CrO_4$, use of published expansion data resulted in disagreement between calculated strain energy values and published, measured $\Delta H_{tr}$ data.

## Introduction

At room temperature $K_2SO_4$ crystallizes with the so-called $\beta$-$K_2SO_4$ structure (space group Pnma-$D_{2h}^{16}$). The positional parameters have been refined by McGinnety [1]. Near 587 °C, the orthorhombic $\beta$-$K_2SO_4$ transforms discontinuously to hexagonal $\alpha$-$K_2SO_4$. The space group of $\alpha$-$K_2SO_4$ is P$6_3$/mmc-$D_{6h}^4$ [2–5]. There is a static, disordered arrangement of the tetrahedral sulfate ions in $\alpha$-$K_2SO_4$. Van den Berg and Tuinstra [2] and Miyake et al. [3] assume that one apex of any $SO_4^{2-}$ ion points randomly (but statically) either up or down along the $\bar{6}$-axis [2, 3]. Arnold et al. [4] agreed to this model for $\alpha$-$K_2SO_4$ at 800 °C. But for temperatures closer to the phase transition they favored the "edge model" (i.e., three equivalent orientations of the sulfate ions which have one O–O edge rather than one S–O bond parallel to the $\bar{6}$-axis) [4].

There is agreement between [2] and [4] as to a split position for one set (K2) out of the two crystallographically independent sets of potassium ions in $\alpha$-$K_2SO_4$ (the K1 ions form chains –K1–K1–K1– along the hexagonal axis; the K2 ions are arranged in chains –K2–$SO_4$–K2–$SO_4$–K2– parallel to the K1 chains). The split position of the K2 ions implies an $R \ln 2$ term for the entropy change associated with the $\beta \rightarrow \alpha$ phase transition. This $R \cdot \ln 2$ term adds to a similar term associated with the disorder of the sulfate ions in the $\alpha$ phase ($R \cdot \ln 2$ in the case of the apex-up/apex-down model of [2] or $R \cdot \ln 3$ in the case of the edge model favored by [4]). Strong correlations between the positions taken by the K2 ions and the orientation of the neighbouring $SO_4^{2-}$ ions have been assumed in [2]. Discussing the packing of ions in the $\alpha$-$K_2SO_4$ type, Fischmeister [7] in an early paper anticipated short range order as an essential feature of that structure type. Short range order has indeed been found by neutron scattering experiments on $\alpha$-$K_2SO_4$. The strong (013) reflection of $\beta$-$K_2SO_4$ is extinct in $\alpha$-$K_2SO_4$. At 867 K, the region of that reflection was scanned on a triple-axes neutron spectrometer, and diffuse, elastic intensity was found (see the contour plot, Fig. 5 in paper [4]).

The correlations existing between the orientations of $SO_4^{2-}$ ions and the occupancies of the split positions of their neighbouring K2 ions reduce the disorder of the $\alpha$-phase, hence the expected entropy of transition, $\Delta S_{tr}$, will be less than $R \cdot (2 \cdot \ln 2)$ or $R \cdot (\ln 2 + \ln 3)$. In addition, the large mean square displacements of the K2 ions in the $\beta$-phase suggest that some disorder develops with the K2 ions already below $T_{tr}$. It is, however, unlikely that $\Delta S_{tr}$ is reduced to a mere $R \cdot \ln 2$. The low value $\Delta S_{tr} = 4.98\ \mathrm{J\,K^{-1}\,mol^{-1}}$ (being less than $R \ln 2$), which was given by [8], presumably is due to problems with the sample studied as discussed below in the section "Enthalpy and Entropy of Transition". To settle this point is of some practical interest since $K_2SO_4$ is widely used as a calibration

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Table 1. Transition enthalpies reported for $K_2SO_4$.

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $T_{tr}$ in K | $855 \pm 1$ | – | 856 | 856 | 856 | 856 | 856.8 | 857 | 857 | 858.5 | 860 | 860 | 868? |
| $\Delta H_{tr}$ in kcal/mol | 2.14<br>$\pm 0.07$ | 2.1 | 1.94 | 1.54 | 1.23 [a] | – | 1.46<br>$\pm 0.90$ | 2.02 | 1.01 [b] | 1.385 | 1.023 | 1.94 | 1.92 |
| $\Delta S_{tr}$ in $cal \cdot mol^{-1} \cdot K^{-1}$ | 2.5<br>$\pm 0.1$ | ~2.3 | 2.26 | (1.8) | 1.44 [a] | – | 1.704 | 2.36 | 1.18 [b] | 1.613 | 1.19 | 2.26 | 2.21 ? |
| Method [c] | cal | DTA | cal | cal | CC | DTA | DSC | cal | CC | – | cal | cal | cal |
| Heating [d] rate in K/s | [e] | ~1/6 | [f] | <1/30 | n.g. | – | +10;<br>−40 | [g] | +1 to<br>+3 | – | n.g. | n.g. | −1/12 [h] |
| Reference | [26, 27] | [37] | [12] | [29] | [11] | [45] | [32] | [13] | [10] | [33] | [8],<br>([31]) | [9] | [28] |

[a] Using the $\Delta V$ value 1.01 $cm^3/mol$ measured by [11]. – [b] Recalculated using the value $\Delta V = 0.9\ cm^3/mol$ value from [4]. – [c] cal: calorimetric, DSC: differential scanning calorimetry, DTA: differential thermal analysis, CC: Clausius-Clapeyron. – [d] + sign: heating; – sign: cooling; n.g.: not given. – [e] Drop-calorimeter (ice) [26]. – [f], [g] Sample dropped into cold Cu block, see [36] p. 3143[f] and [38] p. 270[g], respectively. – [h] Cooling rate of ~5 K/min according to [30] cited in [28].

standard in thermal analysis, where the $\alpha \rightarrow \beta$ transition not only serves to fix the temperature scale but is also used to estimate the magnitude of the heat effects.

A noteworthy feature associated with the $\beta \rightarrow \alpha$ phase transition of $K_2SO_4$ is the observation [4, 6] that a $\beta$-$K_2SO_4$ crystal annealed for 3 days at 847 K (i.e., significantly below the $T_{tr}$ value found at usual thermal scan speeds) had transformed into $\alpha$-$K_2SO_4$ [4, 6].

Optical investigations of the $\alpha \leftrightarrow \beta$ phase transition of $K_2SO_4$ indicated an intermediate phase existing in a narrow temperature range ($\Delta T \approx 7$ K) between $\beta$-$K_2SO_4$ and $\alpha$-$K_2SO_4$ [16, 17, 35]. These optical studies might give some support to the speculations about an intermediate "glassy" phase advanced by Merlin [15].

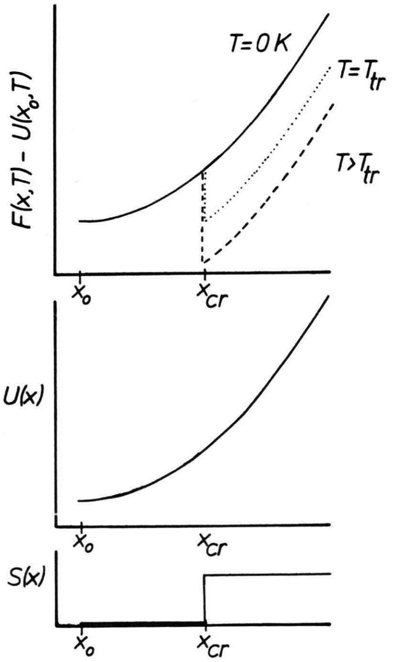

Fig. 1. The order parameter may vanish for $x > x_{cr}$ where the constraint on a particular degree of freedom is released. The entropy, $S(x)$, jumps at $x = x_{cr}$ while the internal energy, $U(x)$, increases continuously. The free energy $F(x, T)$, diminished by $U(x_0, T)$, is minimum for $x = x_0$ for any $T < T_{tr}$. Two equal minimum values occur at $T = T_{tr}$ for $x = x_0$ and $x = x_{cr}$. For $T > T_{tr}$ the absolute minimum of $F(x, T) - U(x_0, T)$ occurs at $x = x_{cr}$.

## Enthalpy and Entropy of Transition

The calorimetrically measured enthalpy change associated with the $\alpha \leftrightarrow \beta$ phase transition of $K_2SO_4$ ranges at $\Delta H_{tr} \approx 2$ kcal/mol, see Table 1. The $\Delta H_{tr} = 1.94$ kcal/mol and the entropy change $\Delta S_{tr} = 2.3$ cal $K^{-1}$ $mol^{-1}$ given by Miyake, Minato and Iwai in [9] agree with the results of other authors. Later, Miyake and Iwai [8] revised their results given in [9] and suggested that the excess specific heat measured around the phase transition should be divided into two parts, a smoothly varying base of the $c_p$ vs. $T$ curve and a spike at $T_{tr}$. The base was attributed to the anharmonic vibrations of $K^+$ ions and $SO_4^{2-}$ tetrahedra. The heat associated with the spike in the $c_p$ vs. $T$ curve was identified as $\Delta H_{tr}$, and Miyake and Iwai [8] arrived at a value of 4.28 kJ/mol for $\Delta H_{tr}$ and to 4.98 J $K^{-1}$ $mol^{-1}$ for $\Delta S_{tr}$ in close agreement with high-pressure DTA studies of the phase diagram evaluated by the Clausius-Clapeyron equation in [10, 11] (see Table 1).

The analysis in [8] is not given in sufficient detail as to assess reliably any possible influence of impurities on the results reported. Shomate and Naylor [12] noted a pretransitional phenomenon close to $T_{tr}$ in their calorimetric study of $K_2SO_4$ [12]. In a search for this effect, Dworkin and Bredig [13] found that it does not exist with pure $K_2SO_4$. Rather, any pretransitional phenomena observed were due to impurities [13]. For the effect of these, see also [14]. Inspection of Fig. 1 of paper [8] suggests that the $c_p$ vs. $T$ curve given in [8] shows a pretransitional phenomenon in the range $T_{tr} - 30\ \mathrm{K} < T < T_{tr}$, possibly caused by impurities (this would not invalidate Miyake's and Iwai's conclusion that anharmonic vibrations contribute to $c_p$ in the range $T_{tr} - 200\ \mathrm{K} < T < T_{tr}$ [8]).

The agreement between the calorimetric $\Delta H_{tr}$ value of 4.28 kJ/mol given in [8] and that from high-pressure DTA [10, 11] appears to be spurious. The many independent $\Delta H_{tr}$ values around 2 kcal/mol determined without use of the Clausius-Clapeyron equation (see Table 1) suggest that the corrections made in [8] are exaggerated. As shown below, in the case of $K_2SO_4$ the Clausius-Clapeyron equation and the slope of the $T_{tr}$ vs. $p$ curve must not be used for $\Delta H_{tr}$ determinations and the $\mathrm{d}T_{tr}/\mathrm{d}p$ values found in [10, 11] and $\Delta H_{tr} \approx 2$ kcal/mol are not really contradictory.

## Limitations to the Clausius-Clapeyron Equation

Standard derivations of the Clausius-Clapeyron equation refer to a cyclic process. On completion of one cycle the latent heat $q$ has been absorbed and a (maximum) work of $(\Delta V) \cdot \mathrm{d}p = q \cdot \eta$ was performed. For the reversible Carnot cycle, performed on an ideal medium, the engine efficiency $\eta$ is $\Delta(\ln T) = T^{-1} \cdot \Delta T$. For any irreversible process the actual engine efficiency is below the Carnot value $T^{-1} \cdot \Delta T$.

With respect to the Carnot cycle, $K_2SO_4$ is a non-ideal medium since compressions and expansions are substantially dissipative near $T_{tr}$. The longitudinal acoustic (LA) phonons propagating along [$h$ 0 0] in (Pnma setting) slow down and are damped when $\beta$-$K_2SO_4$ is heated to temperatures near $T_{tr}$. In $\alpha$-$K_2SO_4$ those LA phonons (propagating along [0 0 $l$] in $P6_3$/mmc) are also slow and damped. The slowing down of the LA phonons propagating along the (pseudo-) hexagonal axis corresponds to a softening of the crystal with respect to compressions and dilatations along that direction. This softening and the damping of LA phonons were revealed by inelastic neutron scattering [6], the softening being corroborated by a re-analysis of published X-ray and neutron *diffraction* data, see the section "Compressibilities", below. In the limit of infinitely long wavelengths, the damping of the LA phonons means dissipation of strain energy in compression-expansion cycles.

The involved task to deconvolute as-measured LA phonon widths into (triple-axes neutron) spectrometer resolution and true phonon width has not been done for $K_2SO_4$. But even without knowing the true phonon width (phonon life time) exactly, the strong temperature dependence of the as-measured LA phonon widths shows that the true width is substantial for LA phonons propagating along the (pseudo-) hexagonal axis. The damping is so strong that the oscillations have gone after a few cycles. A sizeable fraction of the work $(\Delta V) \cdot \mathrm{d}p$ is dissipated in one compression-expansion cycle, and the corresponding engine efficiency is below that of the Carnot process.

This irreversibility of the load-unload cycles near $T_{tr}$ necessarily implies a failure of the Clausius-Clapeyron equation if applied to the $\alpha \leftrightarrow \beta$ phase transition of $K_2SO_4$. Therefore it is not feasible to evaluate the transition enthalpy $\Delta H_{tr}$ for the $\alpha \rightarrow \beta$ transition of $K_2SO_4$ from the $T_{tr}$ vs. $p$ diagram. The $\alpha \leftrightarrow \beta$ phase boundary was determined using high-pressure DTA by [10, 11], and from its slope, $\mathrm{d}p_{tr}/\mathrm{d}T_{tr}$, the $\Delta H_{tr}$ was evaluated by the Clausius-Clapeyron equation using the (high) ideal-process $\eta$ value $T^{-1} \cdot \Delta T$ [10, 11]. The low value obtained for the product $(\Delta H_{tr}) \cdot \eta$, hence, erroneously was ascribed to a low $\Delta H_{tr}$ value.

It appears that consideration of the peculiar lattice dynamics of $K_2SO_4$ (softening near $T_{tr}$ of the crystal for LA phonons and their damping) removes at least part of the disagreement between high-pressure DTA data and calorimetric results.

## Model for Discontinuous Order-Disorder Phase Transitions

This model is developed with reference to the $\beta \rightarrow \alpha$ $K_2SO_4$ phase transition, which is of the order-disorder type with orientationally ordered $SO_4^{2-}$ ions in the $\beta$-phase and disordered ones in the $\alpha$-phase [2–4]. According to the temperature dependence of the lattice parameters, this transition is discontinuous, see, e.g. [6–8, 11, 18]. Both phases co-exist in a single crystal at the phase transition [19]. The thermal expansion is nonlinear along the $a$-axis (Pnma), and the lattice parameter vs. temperature curves indicate a

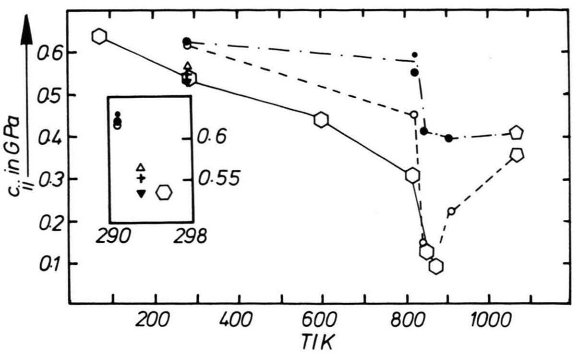

Fig. 2. Plot of the elastic stiffnesses vs. temperature for $K_2SO_4$. The lines drawn are guides to the eye. The $c_{11}$ (open circles and apex-down pentagon), $c_{22}$ (large full circle and apex-up pentagon), and $c_{33}$ (small full circle) are derived from diffraction studies [1, 3, 4] ($c_{22} = c_{33}$ for $T > T_{tr}$). The 291 K data are from the X-ray study [1] and the 1073 K data (pentagons) from the X-ray diffraction study [3]. The 832 K, 847 K, and 913 K data are from neutron diffraction [4]. The hexagons give the $c_{11}$ data from [6] (the moderately sloping $c_{22}$ data from [6] are omitted from this figure for the sake of clarity; they behave much like the diffraction data). The insert shows on an expanded scale near-room temperature data: the 293 K ultrasonic data from [34] for $c_{11}$, $c_{22}$, and $c_{33}$ are indicated by a cross, a full triangle, and an open triangle, respectively [34]. Due to temperature gradients the temperature values in [6] are offset to higher temperatures by as much as 20 K near $T_{tr}$, and the agreement between $c_{ii}$ from dispersion curves [6] and diffraction [1, 3, 4] is actually better than the plotted data suggest.

continuous transition that is abruptly completed by a jump at the transition temperature $T_{tr}$.

The following phenomenological model of discontinuous order-disorder transitions assumes that in the ordered low-temperature phase some internal degree of freedom, $f$, is blocked, being subjected to constraints that are removed by the phase transition. In the case of $K_2SO_4$ this degree of freedom is the orientation of the sulfate ions.

The order-disorder transition involves a change in entropy, $\Delta S$, and is accompanied by a considerable volume expansion, i.e., by a change in an extensive parameter. The entropy may be written as $S = S_0(T) + R \ln(f[x])$ with $x$ = volume, lattice parameter, .... If there is some critical value, $x_{cr}$, such that $f(x) = 1$ for $x < x_{cr}$ and $f(x) = n$ for $x > x_{cr}$, a discontinuous phase change will occur for $x = x_{cr}$.

At low temperatures the lattice parameters of $\beta$-$K_2SO_4$ increase linearly with $T$. Above ~350 °C, the $a$-axis (Pnma) expands more than proportionally to $T$ [6–8, 18]. This suggests to break down the thermal expansion of $K_2SO_4$ into a regular expansion characterized by the expansion coefficients found at low temperatures and into the excess expansion found at the higher temperatures. The regular part accounts for the additional space required for the thermal agitation increasing with temperature. It does not provide for the additional space needed to bring the ordered arrangement of tetrahedra into a disordered condition. Rather, it is the excess expansion and the jump in molar volume at the phase transition that relax the constraint on the orientation of the sulfate ions.

In a fictitious experiment we may conceive the *excess* expansion as brought about by application of stress (in contrast to experiment where this is done by heating). The corresponding increase in elastic energy, $\Delta U$, may be calculated from the elastic constants. In Fig. 1, the $\Delta U$ vs. $x$ relationship is plotted along with $\Delta S$ vs. $x$ schematically for this fictitious experiment. The amplitude of the jump in $S$ depends on the structural details of the disordered phase. For $\alpha$-$K_2SO_4$ the Ising type models used by [2, 3] imply $\Delta S = R \cdot \ln 2$; the model used in [4] yields $R \cdot \ln 3$.

In Fig. 1 also the change in free energy, $\Delta F = \Delta U - T \cdot \Delta S$, is plotted vs. $x$ for various temperatures $T$. Raising $T$ above $T_{cr}$ results in a spontaneous change of state: without application of stress the parameter $x$ jumps from $x = x_0$ to $x = x_{cr}$.

In the following section this model will be tested numerically on the potassium salts $K_2SO_4$, $K_2SeO_4$ and $K_2CrO_4$.

## Comparison with $K_2SO_4$

The lattice parameters of $K_2SO_4$ at 291 K are $a = 7.476$ Å, $b = 5.763$ Å, and $c = 10.071$ Å (setting: Pnma) [1]. According to [34] the coefficients of thermal expansion along these axes are $0.0375 \cdot 10^{-3}$ K$^{-1}$ for $a$ and $b$, and $0.034 \cdot 10^{-3}$ K$^{-1}$ for $c$. With these data the fictitious cell at 847 K has the parameters $a' = 7.632$ Å, $b' = 5.883$ Å, and $c' = 10.261$ Å. The measured parameters at this temperature (above the phase transition) are 8.118 Å, 5.886 Å, and 10.209 Å [4]. (For 620 °C the orthohexagonal lattice parameters $a_{orthex} = 10.25$ Å, $b_{orthex} = 5.92$ Å, $c_{orthex} = 8.13$ Å have been given [45]). The fictitious strains due to the phase transition are $\varepsilon_1 = \Delta a/a' = 0.486/7.632 \approx 0.0637$, $\varepsilon_2 = \Delta b/b' = 0.00284/5.883 \approx 0.00048$, and $\varepsilon_3 = \Delta c/c' = -0.05238/10.261 \approx -0.0051$. Using the elastic constants given in [34] and assuming $\varepsilon_i = 0$ for $i = 4$, 5, and 6, the energy density $u = \frac{1}{2} \sum c_{ij} \varepsilon_i \varepsilon_j \approx 106.6$ J/cm$^3$, corresponding to ~7.74 kJ/mol or ~1.85 kcal/mol, in very good agreement with the $\Delta H_{tr}$ values found experimentally, see Table 1. $T_{tr} \geq \Delta U/\Delta S \approx 1.85$ kcal $\cdot \mathrm{mol}^{-1}/(1.987 \cdot \ln(f)\,\mathrm{cal} \cdot \mathrm{K}^{-1} \cdot \mathrm{mol}^{-1}) \geq 930\,\mathrm{K}/\ln(f)$. For $f=2$ and $f=3$ the calculated $T_{tr}$ is $\geq 1342$ and 847 K, respectively.

Figure 2 compares the $c_{ii}$ values derived from X-ray [3] and neutron [4] diffraction data (see the "Appendix on Compressibilities", below) with results from ultrasonic studies [34] and inelastic neutron scattering work [6].

## Comparison with $K_2SeO_4$

$K_2SeO_4$ shows LA phonon softening along [$h$ 0 0] (setting: Pnam), but no damping was noted in the Brillouin scattering work by Cho and Yagi [24, 25], see also [39]. Thus, high-pressure DTA should yield reliable $\Delta H_{tr}$ values (via the Clausius-Clapeyron equation). The jump in molar volume, $\Delta V$, at the phase transition has not yet been determined exactly. But the space group and lattice parameters are known for both 400 °C and 500 °C. At 400 °C (Pnam), $a=7.85$ Å, $b=10.50$ Å, and $c=6.04$ Å [22]; at 500 °C ($P6_3/mmc$), $a_h=6.077$ Å, and $c_h=8.029$ Å – in orthohexagonal parameters ($b'=\sqrt{3}\,c'$) $a'=8.029$ Å, $b'=10.526$ Å, and $c'=6.077$ Å [23]. By calorimetry, $T_{tr}=734 \pm 5$ K and $\Delta H_{tr}=1.1 \pm 0.1$ kcal/mol [20]. Using the thermal expansion coefficients published by Flerov et al. [21], the $\Delta V$ at ~ 734 K may be estimated at ~1.58 $\mathrm{cm}^3/\mathrm{mol}$. According to Pistorius and Rapoport [10] $\mathrm{d}T_{tr}/\mathrm{d}p=22.65$ K/kbar [10]. This would indicate $\Delta H_{tr} \approx 5.03$ kJ/mol $\approx 1.2$ cal/mol, indicating very good agreement between the $\Delta H_{tr}$ value determined by the Clausius-Clapeyron equation and the calorimetric value 1.1 kcal/mol.

The treatment of the phase transition of $K_2SeO_4$ in terms of the above model for discontinuous order-disorder transitions requires the calculation of the fictitious cell at $T_{tr}$. According to Flerov et al. [21] the thermal expansion of $K_2SeO_4$ is nonlinear already at low temperatures. The regular portion of the expansion would be characterized by the coefficients (in $10^{-6}\,\mathrm{K}^{-1}$) $\alpha_i=17.2$, 37.7 and 23.0 for expansion along $a$, $b$, $c$ (setting: Pnam), respectively [21]. Using the room temperature parameters $a=7.661 \pm 0.004$ Å, $b=10.466 \pm 0.008$ Å, and $c=6.003 \pm 0.003$ Å (setting: Pnam) given in [40], for the fictitious cell at $T_{tr}=734$ K the parameters $a''=7.719$ Å, $b''=10.641$ Å, and $c''=6.064$ Å are calculated. The measured orthohexagonal parameters at 773 K are $a'=8.029$ Å, $b'=10.526$ Å, and $c'=6.077$ Å [23]. The fictitious strains along $a'$, $b'$ and $c'$ are ~0.0402, ~ −0.0014 and ~0.00214, respectively. With the elastic stiffness coefficients $c_{ii}=46.74$, 45.65 and 36.09 GPa (setting: Pnam) read from a figure in [41], p. 3825, an energy density of 0.0378 GPa results corresponding to ~2.84 kJ/mol, considerably less than the calorimetrically measured $\Delta H_{tr}=1.1$ kcal/mol.

$V_{cell}=a \cdot b \cdot c=7.661 \times 6.003 \times 10.466\,\text{Å}^3=481.321\,\text{Å}^3$ [40] and $T=291$ K assumed. The following mean square displacements are given [40]:

| | Se | K(1) | K(2) | O(1) | O(2) | O(3) |
|---|---|---|---|---|---|---|
| $\langle u^2 \rangle$ | 0.0125 | 0.0135 | 0.0164 | 0.0373 | 0.0389 | 0.0474 |
| $\langle v^2 \rangle$ | 0.0172 | 0.0264 | 0.0283 | 0.0465 | 0.0584 | 0.0239 |
| $\langle w^2 \rangle$ | 0.016 | 0.0198 | 0.0295 | 0.0213 | 0.0583 | 0.0417 |

Note: there seems to be a problem with the $\langle v^2 \rangle=0.0239$ Å$^2$ for O(3).

The compressibilities $\varkappa_x$ ($N=7$) ($x=u$, $v$, $w$) and stiffnesses $c_{ii}$ along the $a$-, $b$-, and $c$-axes calculated from the mean square displacements according to the procedure explained in the Appendix are as follows: $\varkappa_x$ (in $10^{-12}\,\mathrm{cm}^3/\mathrm{erg}$) = 1.96, 2.06 and 2.1 for $x=u$, $v$ and $w$, respectively. The corresponding $c_{ii}$ are 51, 48.5, and 47.7 GPa.

## Comparison with $K_2CrO_4$

According to Toriumi and Saito [44] $V_{cell}=471.2$ Å$^3$ ($T=291$ K assumed). The following mean square displacements are given [44]:

| | Cr | K(1) | K(2) | O(1) | O(2) | O(3) |
|---|---|---|---|---|---|---|
| $\langle u^2 \rangle$ | 0.01102 | 0.01709 | 0.01605 | 0.0116 | 0.0253 | 0.0369 |
| $\langle v^2 \rangle$ | 0.01339 | 0.02501 | 0.02449 | 0.0511 | 0.0416 | 0.021 |
| $\langle w^2 \rangle$ | 0.01256 | 0.0289 | 0.01699 | 0.036 | 0.0165 | 0.035 |

Considering only the translational motions of the $CrO_4^{2-}$ ion, i.e., disregarding its librations, the following compressibilities and stiffnesses result for $K_2CrO_4$ (procedure and notation are explained in the Appendix): $\varkappa_x$ (in $10^{-12}\,\mathrm{cm}^3/\mathrm{erg}$) = 1.4, 1.8, and 1.65 for $x=u$, $v$, and $w$, respectively. The corresponding $c_{ii}$ are 71, 55, and 61 GPa. (The data from [1] resulted in $c_{ii}=111$, 42, and 57 GPa for $i=1$, 2, and 3, respectively.)

The compressibility $\varkappa\,(N=7)=4.87\times10^{-12}\,\mathrm{cm}^3/\mathrm{erg}$ or $\varkappa(N=3)=4.67\times10^{-12}\,\mathrm{cm}^3/\mathrm{erg}$.

The lattice parameters of $K_2CrO_4$ are $a=7.666$ Å, $b=5.918$ Å, and $c=10.399$ Å at 20 °C. The orthohexagonal parameters at 680 °C are $a'=8.22$ Å, $b'=6.12$ Å and $c'=10.61$ Å [45].

The thermal expansion of $K_2CrO_4$ has been measured by Pistorius [46]. While $a$ and $c$ expand linearly with $T$, the $b$-parameter expands non-linearly and its temperature variation, measured between 25 and 615 °C may be described by $b=(5.9045+0.000\,59\cdot t-4\times10^{-7}\cdot t^2)$ with $t$ in centigrades. The fictitious cell at 663 °C has the parameters $a_f=7.927$ Å, $b_f=6.12$ Å, and $c_f=10.642$ Å. The strain energy associated with the phase transition is dominated by the contribution due to the strong expansion along $a$: $|\Delta a/a|\approx0.00146$, resulting in an elastic energy density of 3.67 kJ/mol. This value agrees poorly with the Clausius-Clapeyron result $\Delta H=9.5$ kJ/mol (using a volume change of 2.23 cm$^3$/mol and 45.2 bar/K for the pressure dependence of the phase transition [10], revising the 131 bar/K given earlier by Pistorius [46]). The Clausius-Clapeyron result $\Delta H_{\mathrm{tr}}=9.5$ kJ/mol implied by the data of [10] is in very good agreement with the most dependable $\Delta H_{\mathrm{tr}}$ value available, the drop-calorimetrically determined value $2379\pm120$ cal/mol ($\sim9.954\pm0.5$ kJ/mol) [48]. The thermal expansion data given in [46] are in poor agreement with the cubic expansion coefficients of $\sim10^{-4}$/K measured earlier (see, e.g., [47]). According to those earlier data the expansion found by Pistorius [46] along $b$ is too large by about an order of magnitude (near room temperature). Future improved expansion data might ameliorate the agreement between the $\Delta H_{\mathrm{tr}}$ values measured in [48] and the strain energy values from diffraction data.

## Conclusions

To the best of our knowledge $K_2SO_4$ is unique in showing strongly damped soft longitudinal acoustic phonons. This damping of LA phonons that soften in $K_2SO_4$ on approaching the phase transition implies a failure of the Clausius-Clapeyron relationship, which holds only for reversible processes. (No such failure is caused by the damping of *transverse* soft modes associated with phase transitions as TA modes are not directly coupled to external pressure). The disagreement between the heat of transition of $K_2SO_4$ determined calorimetrically on one hand, and from the slope of the $\alpha-\beta$ phase boundary in the $p-T$ diagram on the other hand, is traced back to the failure of the Clausius-Clapeyron relationship indicated above. $\Delta H_{\mathrm{tr}}\approx2$ kcal/mol.

Anisotropic thermal displacement parameters now routinely determined in crystal structure research provide fairly reliable elastic stiffness constants $c_{ii}$ ($i=1$, 2, 3). This is demonstrated for $K_2SO_4$ by a comparison of the temperature dependence of the $c_{ii}$ evaluated from phonon dispersion curves and values derived from displacement parameters determined by X-ray and neutron diffraction. Stiffness values estimated from diffraction data may be of value in cases where conventional methods of $c_{ii}$ measurement fail (e.g., for lack of crystals of sufficient size or appropriate shape). Conversely, in cases where the $c_{ii}$ are known from conventional techniques a comparison with diffraction derived $c_{ii}$ values might help to settle whether anomalous Debye-Waller factors are due to static displacements (e.g., split atom positions), artefacts of the refinement (e.g., undetected twinning of the crystal studied), or dynamical disorder.

The model presented interrelates the phase transition temperature, the heat of transition, and the strain energy and consistently describes the discontinuous order-disorder transition of $K_2SO_4$.

## Appendix on Compressibilities

This section describes the calculation of approximate compressibilities $\varkappa$ from the thermal parameters ("temperature factors") determined by diffraction methods. It is well known that the accuracy of temperature factors ranges at $\sim10\%$ even for structure determinations yielding positional parameters accurate to $\sim0.01\%$. Nonetheless, estimates fo $\varkappa$ derived from diffraction data may prove useful in cases where conventional $\varkappa$ data are not available.

In the harmonic approximation and for a simple cubic lattice with one atom per unit cell, the mean square displacement $\langle u^2\rangle$ along one axis is related to the force constant $\alpha$ by $\alpha\cdot\langle u^2\rangle=k_BT$. The force constant $\alpha$ is related to the compressibility $\varkappa$ and to the lattice parameter $a$ by $\varkappa=3a/\alpha$, see [42]. Thus, $\varkappa$ is related to the mean square displacement $\langle u^2\rangle$ by $\varkappa=(3a\cdot\langle u^2\rangle)/(k_BT)$. With $\langle u^2\rangle$, $\langle v^2\rangle$ and $\langle w^2\rangle$ denoting the mean square displacements along the $a$, $b$, and $c$ axes, we may write

$$\varkappa=(a\cdot b\cdot c)^{1/3}\cdot(\langle u^2\rangle+\langle v^2\rangle+\langle w^2\rangle/(k_BT)$$

for one atom per unit cell. For orthorhombic cells with $N$ equal atoms, the following generalization is assumed to hold:

$$\varkappa \cdot (k_B T) = (V_{\text{cell}}/N)^{1/3} \cdot (1/N) \cdot \Sigma_i(\langle u_i^2 \rangle + \langle v_i^2 \rangle + \langle w_i^2 \rangle), \quad (i = 1, \ldots, N).$$

This form is suggested by the fact that the physics must not change by switching from a description in terms of a primitive cell to a description in terms of a larger cell.

Ideally, one would use the displacement parameters of all of the atoms present in the cell. The data of one or more sets of atoms might, however, be unreliable. For instance, diffraction data do not distinguish between displacements due to static disorder and thermal displacements. In such cases it is advisable to disregard the set of atoms with doubtful parameters and to keep only the certain ones. For instance, in $K_2SeO_4$ disorder develops already below $T_{\text{tr}}$ and flipped $SeO_4$ tetrahedra have been observed by neutron diffraction. The fraction of tetrahedra with "wrong" orientation was 9% at room temperature and 15% at 400 °C [22] (50% would mean full disorder). In this case it is obviously better to use the parameters of only three atoms ("$N=3$"), namely of K 1, K 2 and of the center of gravity of the $SeO_4$ group, Se, rather than to use the full set ("$N=7$") of K 1, K 2, Se, O 1, O 2, and (2 ×) O 3.

The sulfate *groups* in $K_2SO_4$ may be considered as rigid bodies (the internal vibrations of the sulfate ion have wavenumbers of 447 $\text{cm}^{-1}$ and higher, see [43]). These rigid groups have translational and rotational degrees of freedom (three generalized positions and three generalized velocities for both translation and rotation). In the context of $\varkappa$ determinations one might disregard the mean square displacements due to $SO_4^{2-}$ librations in as much as these librations are "disconnected" from the translations. The librations may, however, be important with respect to "plastic phase" behavior.

The results may be compared with the compressibility and the stiffnesses $c_{ii}$ ($i=1, 2, 3$) obtained at room temperature in [34] by conventional ultrasonic techniques and with the $c_{ii}$ determined from the slope of phonon dispersion curves measured at various temperatures by inelastic neutron scattering, see [6]. The success of the method presented is illustrated by Figure 2. Therefore, this method might be used conversely also in cases where the elastic constants are known but the displacement factors are subject to doubt. It might help to decide whether these are due only to thermal motion or whether they in addition reflect static disorder, split atom positions, or the like.

The mean square displacements (in Å²) of the K(1), K(2), O(1), O(2), O(3), and S atoms in $\beta$-$K_2SO_4$ are given for $T=291$ K in the table below using X-ray data from [1]: setting: Pnma (the atom labels K 1 and K 2 are interchanged with respect to paper [1])

| | S | K(1) | K(2) | O(1) | O(2) | O(3) |
|---|---|---|---|---|---|---|
| $\langle u^2 \rangle$ | 0.01569 | 0.02322 | 0.02025 | 0.01821 | 0.03228 | 0.03794 |
| $\langle v^2 \rangle$ | 0.01457 | 0.02142 | 0.02265 | 0.03348 | 0.02743 | 0.01868 |
| $\langle w^2 \rangle$ | 0.01444 | 0.02425 | 0.01922 | 0.03443 | 0.0149 | 0.02826 |

The compliances $\varkappa_x$ ($x=u, v, w$) are given by

$$\varkappa_x = (V_{\text{cell}}/Z \cdot N)^{1/3} \cdot (Z \cdot N)^{-1} \cdot (\Sigma_i \langle x_i^2 \rangle)/(k_B T), \quad (i = 1, \ldots, Z \cdot N).$$

For $T=291$ K, $\varkappa_x$ (in $10^{-12}$ cm³/erg) is calculated from the X-ray diffraction data (from [1]) considering only the K(1), K(2), and S atoms ($N=3$) as $\varkappa_u=1.62$, $\varkappa_v=1.61$ and $\varkappa_w=1.59$, and the elastic stiffnesses $c_{ii}$ $(=\varkappa_i^{-1})$ are $c_{11}=61.6$ GPa, $c_{22}=62.2$ GPa, and $c_{33}=62.9$ GPa.

For $T=832$ K, $\varkappa_x$ (in $10^{-12}$ cm²/erg) is calculated from the neutron diffraction data (from [4]) considering only the K(1), K(2), and S atoms as $\varkappa_u=2.19$, $\varkappa_v=1.80$, and $\varkappa_w=1.68$. The elastic stiffnesses $c_{ii}$ $(=\varkappa_i^{-1})$ are calculated as $c_{11}=45.7$ GPa, $c_{22}=55.6$ GPa, and $c_{33}=59.5$ GPa.

For $T=847$ K, $\varkappa_x$ (in $10^{-12}$ cm³/erg) is calculated for $N=3$ from the neutron diffraction data (edge model, from [4]) as $\varkappa_u=6.35$, $\varkappa_v=\varkappa_w=2.39$. The $c_{ii}$ $(=\varkappa_i^{-1})$ are $c_{11}=15.8$ GPa and $c_{22}=c_{33}=41.8$ GPa.

For $T=913$ K, the edge model yields $\varkappa_x$ (in $10^{-12}$ cm³/erg) for $N=3$ from the neutron diffraction data (from [4]) as $\varkappa_u=4.51$, $\varkappa_v=\varkappa_w=2.52$. The resulting $c_{ii}$ $(=\varkappa_i^{-1})$ are $c_{11}=22.2$ GPa and $c_{22}=c_{33}=39.7$ GPa.

For $T=1073$ K, $\varkappa_x$ (in $10^{-12}$ cm³/erg) was calculated for $N=3$ from the X-ray diffraction data (from [3]) assuming the edge model: $\varkappa_u=2.79$, $\varkappa_v=\varkappa_w=2.45$. The $c_{ii}$ $(=\varkappa_i^{-1})$ are calculated as $c_{11}=35.8$ GPa and $c_{22}=c_{33}=40.8$ GPa.

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