The Phase Transition of Potassium Sulfate

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The discontinuous phase transition of K₂SO₄ is described by a semi-empirical model that uses the elastic stiffnesses cᵢ 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 K₂SO₄ removes the disagreement between transition enthalpies ΔHₑ and measured calorimetrically and ΔHₑ derived from the p-T phase diagram via the Clausius-Clapeyron equation. The model used requires the knowledge of the cᵢ (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 ΔHₑ also for K₂SeO₄. In the case of K₂CrO₄, use of published expansion data resulted in disagreement between calculated strain energy values and published, measured ΔHₑ data.

Introduction

At room temperature K₂SO₄ crystallizes with the so-called β-K₂SO₄ structure (space group Pnma-D₁₆h⁴). The positional parameters have been refined by McGinney [1]. Near 587 °C, the orthorhombic β-K₂SO₄ transforms discontinuously to hexagonal α-K₂SO₄. The space group of α-K₂SO₄ is P6₃/mmc-D₃h [2–5]. There is a static, disordered arrangement of the tetrahedral sulfate ions in α-K₂SO₄. Van den Berg and Tuinstra [2] and Miyake et al. [3] assume that one apex of any SO₄⁴⁻ ion points randomly (but statistically) either up or down along the 6-axis [2, 3]. Arnold et al. [4] agreed to this model for α-K₂SO₄ 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 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 α-K₂SO₄ (the K₁ ions form chains K₁−K₁−K₁−along the hexagonal axis; the K₂ ions are arranged in chains K₂−SO₄−K₂−SO₄−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 β → α phase transition. This R · ln 2 term adds to a similar term associated with the disorder of the sulfate ions in the α phase (R · ln 2 in the case of the apex-up/ apex-down model of [2] or R · 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 SO₄⁴⁻ ions have been assumed in [2]. Discussing the packing of ions in the α-K₂SO₄ 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 α-K₂SO₄. The strong (013) reflection of β-K₂SO₄ is extinct in α-K₂SO₄. 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 SO₄⁴⁻ ions and the occupancies of the split positions of their neighbouring K₂ ions reduce the disorder of the α-phase, hence the expected entropy of transition, ΔSₑ, will be less than R · ln 2 or R · ln (2 + ln 3). In addition, the large mean square displacements of the K₂ ions in the β-phase suggest that some disorder develops with the K₂ ions already below Tₑ. It is, however, unlikely that ΔSₑ is reduced to a mere R · ln 2. The low value ΔSₑ = 4.98 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 K₂SO₄ is widely used as a calibration

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Table 1. Transition enthalpies reported for K$_2$SO$_4$.

<table>
<thead>
<tr>
<th>$T_{tr}$ in K</th>
<th>$\Delta H_{tr}$ in kcal/mol</th>
<th>$\Delta S_{tr}$ in cal · mol$^{-1}$ · K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>855 ± 1</td>
<td>2.14 ± 0.07</td>
<td>2.5 ± 0.1</td>
</tr>
<tr>
<td>856</td>
<td>2.1</td>
<td>~2.3</td>
</tr>
<tr>
<td>856</td>
<td>1.94</td>
<td>2.26</td>
</tr>
<tr>
<td>856</td>
<td>1.54</td>
<td>(1.8)</td>
</tr>
<tr>
<td>856.8</td>
<td>1.23 ± 0.90</td>
<td>1.44 ± 0.9</td>
</tr>
<tr>
<td>857</td>
<td>1.46</td>
<td>1.704</td>
</tr>
<tr>
<td>857.8</td>
<td>2.02</td>
<td>2.36</td>
</tr>
<tr>
<td>860</td>
<td>1.01</td>
<td>1.18 b</td>
</tr>
<tr>
<td>868</td>
<td>1.385</td>
<td>1.613</td>
</tr>
<tr>
<td>860</td>
<td>1.23</td>
<td>1.19</td>
</tr>
<tr>
<td>860</td>
<td>1.23</td>
<td>2.26</td>
</tr>
<tr>
<td>868</td>
<td>1.23</td>
<td>2.21</td>
</tr>
</tbody>
</table>


Heating rate in K/s: ~1/6, <1/30, +10, 40, +1 to +3, n.g.

Reference: [26, 27] [37] [12] [29] [11] [45] [32] [13] [10] [33] [8], [9], [28]

* Using the AV value 1.01 cm$^3$/mol measured by [11].

- Recalculated using the AV value 1.9 cm$^3$/mol from [4].
- Heating: + sign: heating; — sign: cooling; n.g.: not given.

Enthalpy and Entropy of Transition

The calorimetrically measured enthalpy change associated with the $\alpha \rightarrow \beta$ phase transition of K$_2$SO$_4$ 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 \( T_{tr} \) to \( T \) possibly caused by impurities (this would not invalidate Miyake's and Iwai's conclusion that anharmonic vibrations contribute to \( c_p \) in the range \( T_{tr} \) to \( T \) [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 \( dT_{tr}/dp \) 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 \((\Delta V) \cdot dp = q \cdot \eta \) 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 \((\text{Pnma setting})\) 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 \(\text{P6}_3/\text{mmc}\)) 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 \((\Delta V) \cdot dp \) 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 \( \alpha \leftrightarrow \beta \) 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, \( dp_{tr}/dT_{tr} \), 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 K₂SO₄. 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 $T > T_c$). 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 inset 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 $T_c$, and the agreement between $c_{ij}$ from dispersion curves [6] and diffraction [1, 3, 4] is actually better than the plotted data suggest.

A continuous transition that is abruptly completed by a jump at the transition temperature $T_c$. 

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 K₂SO₄ 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 $\beta$-K₂SO₄ increase linearly with $T$. Above ~ 350 °C, the $a$-axis (Pnmn) expands more than proportionally to $T$ [6–8, 18]. This suggests to break down the thermal expansion of K₂SO₄ 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 $\alpha$-K₂SO₄ 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 K₂SO₄, K₂SeO₄ and K₂CrO₄.

Comparison with K₂SO₄

The lattice parameters of K₂SO₄ 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 · 10⁻³ K⁻¹ for $a$ and $b$, and 0.034 · 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 $e_1 = \Delta a/a = 0.486/7.632 \approx 0.0637$, $e_2 = \Delta b/b = 0.00284/5.883 \approx 0.0048$, and $e_3 = \Delta c/c' = -0.05238/10.261 \approx -0.0051$. Using the elastic constants given in [34] and assuming $e_i = 0$ for $i = 4$, 5, and 6, the energy density $u = \frac{1}{2} \sum c_{ij} e_i e_j \approx 106.6$ J/cm³, 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 mol$^{-1}$/1.987 \cdot \ln(f)$ cal \cdot K$^{-1}$ \cdot mol$^{-1}$ $\geq 930$ K/ln(f). For $f=2$ and $f=3$ the calculated $T_{tr}$ is $\geq 1342$ and 847 K, respectively.

Figure 2 compares the $c_{ij}$ 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, $AV$, at the phase transition has not yet been determined exactly. But according to Pistorius and Rapoport [10] $\nu_{tr}$

$\alpha_{tr}$, $\beta_{tr}$, and $\gamma_{tr}$ are 51, 48.5, and 61 GPa. (The data from [1] resulted in $\alpha_{tr}=111, 42, \text{and } 57$ GPa for $i=1, 2, \text{and } 3$, respectively.)

The compressibilities $c_{ii}$ along the $a$, $b$, and $c$-axes calculated from the mean square displacements according to the procedure explained in the Appendix are as follows: $c_{ii}$ (in $10^{-12}$ cm$^3$/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]:

<table>
<thead>
<tr>
<th></th>
<th>Se</th>
<th>K(1)</th>
<th>K(2)</th>
<th>O(1)</th>
<th>O(2)</th>
<th>O(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle u^2 \rangle$</td>
<td>0.0125</td>
<td>0.0135</td>
<td>0.0164</td>
<td>0.0373</td>
<td>0.0389</td>
<td>0.0474</td>
</tr>
<tr>
<td>$\langle v^2 \rangle$</td>
<td>0.0172</td>
<td>0.0264</td>
<td>0.0283</td>
<td>0.0465</td>
<td>0.0584</td>
<td>0.0239</td>
</tr>
<tr>
<td>$\langle w^2 \rangle$</td>
<td>0.016</td>
<td>0.0198</td>
<td>0.0295</td>
<td>0.0213</td>
<td>0.0583</td>
<td>0.0417</td>
</tr>
</tbody>
</table>

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

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): $x_1$ (in $10^{-12}$ cm$^3$/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 $c_{ii}=111, 42, \text{and } 57$ GPa for $i=1, 2, \text{and } 3$, respectively.)
The compressibility \( \kappa (N = 7) = 4.87 \times 10^{-12} \text{cm}^3/\text{erg} \)
or \( \kappa (N = 3) = 4.67 \times 10^{-12} \text{cm}^3/\text{erg} \).

The lattice parameters of \( \text{K}_2\text{CrO}_4 \) are \( a = 7.666 \text{Å}, b = 5.918 \text{Å}, \) and \( c = 10.399 \text{Å} \) at 20 °C. The ortho-
hexagonal parameters at 680 °C are \( a' = 8.22 \text{Å}, b' = 6.12 \text{Å}, \) and \( c' = 10.61 \text{Å} \) [45].

The thermal expansion of \( \text{K}_2\text{CrO}_4 \) has been mea-
sured 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 \( b = (5.9045 + 0.00059 \cdot t
- 4 \times 10^{-7} \cdot t^2) \) with \( t \) in centigrades. The fictitious cell
at 663 °C has the parameters \( a_t = 7.927 \text{Å}, b_t = 6.12 \text{Å}, \)
and \( c_t = 10.642 \text{Å} \). The strain energy associated with
the phase transition is dominated by the contribution
due to the strong expansion along \( a \): \( |\Delta a/a| \approx 0.00146, \)
resulting in an elastic energy density of 3.67 \text{kJ/mol}.

This value agrees poorly with the Clausius-Clapeyron
result \( \Delta H = 9.5 \text{kJ/mol} \) (using a volume change of
2.23 \text{cm}^3/mol and 45.2 bar/K for the pressure depen-
dence of the phase transition [10], revising the
131 bar/K given earlier by Pistorius [46]). The Clau-
sius-Clapeyron result \( \Delta H_t = 9.5 \text{kJ/mol} \) implied by
the data of [10] is in very good agreement with the most
dependable \( \Delta H_t \) value available, the drop-
calorimetrically determined value \( 2379 \pm 120 \text{cal/mol} \)
(\( \approx 9.954 \pm 0.5 \text{kJ/mol} \) [48]. The thermal expansion
data given in [46] are in poor agreement with the cubic
expansion coefficients of \( \approx 10^{-4} /K \) measured earlier
(see, e.g., [47]). According to those earlier data the ex-
pansion 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 \( \Delta H_t \) values measured in
[48] and the strain energy values from diffraction data.

**Conclusions**

To the best of our knowledge \( \text{K}_2\text{SO}_4 \) is unique in
showing strongly damped soft longitudinal acoustic phonons. This damping of LA phonons that soften in
\( \text{K}_2\text{SO}_4 \) 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 asso-
ciated with phase transitions as TA modes are not
directly coupled to external pressure). The disagree-
ment between the heat of transition of \( \text{K}_2\text{SO}_4 \) deter-
mined 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. \( \Delta H_t \)
\( \approx 2 \text{kcal/mol} \).

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 \( \text{K}_2\text{SO}_4 \) 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 esti-
\mbox{mated 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 appropri-
ate 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), arte-
facts of the refinement (e.g., undetected twinning of the
crystal studied), or dynamical disorder.

The model presented interrelates the phase transi-
tion temperature, the heat of transition, and the strain
energy and consistently describes the discontinuous
order-disorder transition of \( \text{K}_2\text{SO}_4 \).

**Appendix on Compressibilities**

This section describes the calculation of approxi-
mate compressibilities \( \kappa \) from the thermal parameters
("temperature factors") determined by diffraction
methods. It is well known that the accuracy of temper-
ature factors ranges at \( \approx 10\% \) even for structure deter-
minations yielding positional parameters accurate to
\( \approx 0.01\% \). Nonetheless, estimates for \( \kappa \) derived from
diffraction data may prove useful in cases where con-
tventional \( \kappa \) 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 \( \kappa \) by \( \kappa \cdot \langle u^2 \rangle = k_B T \). The force con-
stant \( \kappa \) is related to the compressibility \( \kappa \) and to the
lattice parameter \( a \) by \( \kappa = 3a/\kappa, \) see [42]. Thus, \( \kappa \)
is related to the mean square displacement \( \langle u^2 \rangle \) by
\( \kappa = (3a \cdot \langle u^2 \rangle) / (k_B T) \). With \( \langle u^2 \rangle, \langle v^2 \rangle \) and \( \langle w^2 \rangle \) den-
noting the mean square displacements along the \( a, b, \)
and \( c \) axes, we may write

\[
\kappa = (a \cdot b \cdot c)^{1/3} \cdot (\langle u^2 \rangle + \langle v^2 \rangle + \langle w^2 \rangle) / (k_B T)
\]
for one atom per unit cell. For orthorhombic cells with \( N \) equal atoms, the following generalization is assumed to hold:

\[
x \cdot (k_B T) = (V_{\text{cell}}/N)^{1/3} \cdot (1/N) \cdot \Sigma_i (\langle u_i^2 \rangle + \langle v_i^2 \rangle + \langle w_i^2 \rangle),
\]

\( (i = 1, \ldots, N) \).

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 \( K_2\text{SeO}_4 \) disorder develops already below \( T_r \) and flipped \( \text{SeO}_4 \) 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 K1, K2 and of the center of gravity of the \( \text{SeO}_4 \) group, Se, rather than to use the full set (“N = 7”) of K1, K2, Se, O1, O2, and (2 \( \times \)) O3.

The sulfate groups in \( K_2\text{SeO}_4 \) may be considered as rigid bodies (the internal vibrations of the sulfate ion have wavenumbers of 447 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 \( \kappa \) determinations one might disregard the mean square displacements due to \( \text{SO}_4^{2-} \) 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 \( c_{ij} (i = 1, 2, 3) \) obtained at room temperature in [34] by conventional ultrasonic techniques and with the \( c_{ij} \) 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 Å\(^2\)) of the K(1), K(2), O(1), O(2), O(3), and S atoms in \( \beta-K_2\text{SO}_4 \) are given for \( T = 291 \) K in the table below using X-ray data from [1]: setting: Pnma (the atom labels K1 and K2 are interchanged with respect to paper [1]).

| \( \langle u^2 \rangle \) | 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 \( \kappa_x (x = u, v, w) \) are given by

\[
\kappa_x = (V_{\text{cell}}/Z \cdot N)^{1/3} \cdot (Z \cdot N)^{-1} \cdot (\Sigma_i (\langle \chi_i^2 \rangle)/(k_B T)),
\]

\( (i = 1, \ldots, Z \cdot N) \).

For \( T = 291 \) K, \( \kappa_x \) (in \( 10^{-12} \) cm\(^3\)/erg) is calculated from the X-ray diffraction data (from [1]) considering only the K(1), K(2), and S atoms (\( N = 3 \)) as \( \kappa_u = 1.62, \kappa_v = 1.61 \) and \( \kappa_w = 1.59 \), and the elastic stiffnesses \( c_{ij} (= \kappa_i^{-1}) \) are \( c_{11} = 61.6 \) GPa, \( c_{22} = 62.2 \) GPa, and \( c_{33} = 62.9 \) GPa.

For \( T = 832 \) K, \( \kappa_x \) (in \( 10^{-12} \) cm\(^3\)/erg) is calculated from the neutron diffraction data (from [4]) considering only the K(1), K(2), and S atoms as \( \kappa_u = 2.19, \kappa_v = 1.80, \) and \( \kappa_w = 1.68 \). The elastic stiffnesses \( c_{ij} (= \kappa_i^{-1}) \) are calculated as \( c_{11} = 45.7 \) GPa, \( c_{22} = 55.6 \) GPa, and \( c_{33} = 51.5 \) GPa.

For \( T = 847 \) K, \( \kappa_x \) (in \( 10^{-12} \) cm\(^3\)/erg) is calculated from the neutron diffraction data (edge model, from [4]) as \( \kappa_u = 6.35, \kappa_v = \kappa_w = 2.39. \) The \( c_{ij} (= \kappa_i^{-1}) \) are \( c_{11} = 15.8 \) GPa and \( c_{22} = c_{33} = 41.8 \) GPa.

For \( T = 913 \) K, the edge model yields \( \kappa_x \) (in \( 10^{-12} \) cm\(^3\)/erg) for \( N = 3 \) from the neutron diffraction data (from [4]) as \( \kappa_u = 4.51, \kappa_v = \kappa_w = 2.52. \) The resulting \( c_{ij} (= \kappa_i^{-1}) \) are \( c_{11} = 22.2 \) GPa and \( c_{22} = c_{33} = 39.7 \) GPa.

For \( T = 1073 \) K, \( \kappa_x \) (in \( 10^{-12} \) cm\(^3\)/erg) was calculated for \( N = 3 \) from the X-ray diffraction data (from [3]) assuming the edge model: \( \kappa_u = 2.79, \kappa_v = \kappa_w = 2.45. \) The \( c_{ij} (= \kappa_i^{-1}) \) are calculated as \( c_{11} = 35.8 \) GPa and \( c_{22} = c_{33} = 40.8 \) GPa.