

Structural changes accompanying the phase transformation between leadhillite and susannite: A structural study by means of in situ high-temperature single-crystal X-ray diffraction

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ABSTRACT

To study the temperature-dependent structural changes accompanying the phase transformation leadhillite \leftrightarrow susannite and to verify the close structural relationships between heated leadhillite and susannite, a leadhillite crystal has been investigated by X-ray single-crystal diffraction methods within the temperature range 25–100 °C. The values of the unit-cell parameters were determined at 25, 32, 35, 37, 40, 42, 45, 48, 50, 53, 56, 59, 62, 65, 68, 71, 75, 79, 82, 85, 90, 95, and 100 °C. After the heating experiment the crystal was cooled over the same temperature intervals and the unit-cell dimensions were determined again. The values measured with both increasing and decreasing temperature are in excellent agreement, indicating that no hysteresis occurs within the temperature range examined and that the phase transformation is completely reversible in character. Analysis of the components of the spontaneous strain shows only normal thermal expansion up to 50 °C and that the structural distortions leading to the topology of the heated leadhillite take place in the temperature range 50–82 °C. Our study confirms that the crystal structure of heated leadhillite is topologically identical to that of susannite and that the slight structural changes occurring during the phase transformation leadhillite \leftrightarrow susannite are mainly restricted to the sulfate sheet. Changes in the orientation of sulfate tetrahedra and in the Pb-O coordination polyhedra occur in a continuous way within the temperature range investigated as indicated by the second-order character of the phase transition. In this way, the leadhillite structure gradually goes toward that of susannite without abrupt structural changes.

INTRODUCTION

The minerals of the leadhillite group (Strunz and Nickel 2001), susannite, macphersonite, and leadhillite, are trimorphs of $\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2$. Susannite and leadhillite were discovered more than 150 years ago (Hintze 1930), while macphersonite, the rarest, is much more recent (Livingstone and Sarp 1984). Basically, their crystal structures [space group $P3$ for susannite (Steele et al. 1999); $Pcab$ for macphersonite (Steele et al. 1998); $P2_1/a$ for leadhillite (Giuseppetti et al. 1990)] consist of three kinds of layers: the A layer is composed of SO_4 tetrahedra, the B layer of Pb polyhedra and OH ions, and the C layer by Pb polyhedra and CO_3 groups. Steele et al. (1999) pointed out that the layers are arranged in the stacking sequence ...ABC-CBABCCB... parallel to (001) in leadhillite and macphersonite and to (0001) in susannite, and that the difference between the trimorphs is the relative orientation of the SO_4 tetrahedra within the A layer. In addition these authors determined that the two C layers are equivalent to a slab of cerussite.

One of the most interesting features of these minerals is the reversible phase transformation between leadhillite and susannite (Mrose and Christian 1969). This structural transformation, occurring at about 80 °C, has been studied by means of infrared spectroscopy, thermal analysis, hot-stage microscopy, and powder diffraction (Russell et al. 1984; Milodowski and Morgan 1984; Giuseppetti et al. 1990). The reversible character of the

phase transformation clearly indicates that the structural differences between leadhillite and susannite are very small and the transformation probably displacive. However, Milodowski and Morgan (1984) showed that the susannite resulting from the heating of leadhillite is unstable and, just after cooling at 7 °C, it first converts into a metastable phase, which then reverts into leadhillite. The formation of the intermediate metastable phase was inferred by a peak at 35 °C in the DSC curve (Milodowski and Morgan 1984).

In this light, we decided to study the temperature-dependent structural changes accompanying the phase transformation and to verify the close structural relationships between heated leadhillite and susannite. For this purpose a leadhillite crystal from the Chah Mileh mine, Anarak District, Esfahan Province, Iran (cat. nr. 45948/G, kindly supplied by the Museo di Storia Naturale, Università di Firenze), was studied by means of in situ single-crystal X-ray diffraction in the temperature range 25–100 °C.

EXPERIMENTAL METHOD

A crystal (80 × 100 × 140 μm) of leadhillite was mounted on a Bruker P4 single-crystal diffractometer (MoK α radiation) equipped with a heating device. The temperature of the heater was controlled with a chromel-alumel thermocouple (K-type) placed at the same position where the crystal was located. The temperature fluctuations were less than ± 1.5 °C throughout the temperature range. Unit-cell parameters, determined by centering 25 reflections ($12 < \theta < 15^\circ$) at room temperature, are: $a = 9.104(2)$, $b = 20.792(6)$, $c = 11.577(3)$ Å, $\beta = 90.50(2)$, $V = 2191.3(9)$ Å³. To analyze the structure of leadhillite at room temperature, intensity data were collected up to $\theta = 28^\circ$ (Table 1). Subsequently, the temperature was raised to 32 °C with a heating rate of 1 K/min and the reflections were centered again. The same procedure was then repeated at 35, 37, 40, 42, 45, 48, 50, 53,

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TABLE 1. Experimental details

	leadhillite	heated leadhillite
Temperature (°C)	25	82
space group	<i>P2₁/a</i>	<i>P3</i>
cell parameters	<i>a</i> = 9.104(2) (Å) <i>b</i> = 20.792(6) (Å) <i>c</i> = 11.577(3) (Å) β = 90.50(2)° <i>V</i> = 2191.3(9) (Å ³) <i>Z</i> = 8	<i>a</i> = 9.077(8) (Å) <i>c</i> = 11.611(9) (Å) <i>V</i> = 828(1) (Å ³) <i>Z</i> = 3
chemical formula	Pb ₄ (SO ₄)(CO ₃) ₂ (OH) ₂	Pb ₄ (SO ₄)(CO ₃) ₂ (OH) ₂
wavelength	MoK α (28 mA \times 50 kV)	MoK α (28 mA \times 50 kV)
2 θ range (°)	2–56	2–46
scan mode	ω	ω
scan width (°)	2.60	3.00
variable scan speed (°/min)	1.50/8.00	1.50/6.00
ranges of <i>h, k, l</i>	$\bar{1}, 2, 12; \bar{2}, 7, 27; 0, 15$	$\bar{7}, 7; \bar{7}, 7; 0, 11$
no. of collected refl.	11153	1539
independent refl.	5287	553
refl. with $F_o > 4\sigma(F_o)$	2653	506
<i>R</i> _{merge} (%)	3.01	4.58
<i>R</i> _{obs} (%)	2.49	6.00
<i>R</i> _{all} (%)	2.71	6.76

56, 59, 62, 65, 68, 71, 75, 79, 82, 85, 90, 95, and 100 °C (Table 2a). Before each measurement the sample was held at the specified temperature for 60 min. After the heating experiment, the crystal was cooled over the same temperature intervals and the unit-cell dimensions were again determined (Table 2b).

To determine the crystal structure of heated leadhillite [*a* = 9.077(8), *b* = 20.962(21), *c* = 11.611(9) Å, β = 90.00(7), *V* = 2209(4) Å³ in the monoclinic setting and *a* = 9.077(8), *c* = 11.611(9) Å, *V* = 828(1) Å³ in the trigonal one], we carried out a data collection at 82 °C up to $\theta = 23^\circ$ (Table 1). Collected intensity data were treated for Lorentz-polarization effects and subsequently corrected for absorption following the semi-empirical method of North et al. (1968).

Crystal structure refinement

The full-matrix least-squares program SHELXL-97 (Sheldrick 1997) was used for the refinement of the structures based on *F*². Neutral scattering curves for Pb, S, C, and O were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton 1974).

Leadhillite

The positional parameters of leadhillite reported by Giuseppetti et al. (1990) were used as starting parameters for the room-temperature refinement of the structure. Convergence was quickly achieved for an anisotropic model for all the atoms giving *R* = 2.49% for 2653 observed reflections [$F_o > 4\sigma(F_o)$] and 2.71% for all 5287 independent reflections.

Heated leadhillite (susannite)

Since there is close similarity between heated leadhillite and susannite (Russell et al. 1984; Milodowski and Morgan 1984; Giuseppetti et al. 1990) we decided to use the atomic coordinates reported by Steele et al. (1999) for the *P3* susannite structure as starting parameters. Unfortunately, it was impossible to refine the anisotropic displacement parameters (ADP) for all the atoms because some ADP were non-positive definite. Therefore, isotropic displacement parameters were assumed and refined for all the atoms. Convergence was quickly achieved, giving *R* = 6.00% for 506 observed reflections [$F_o > 4\sigma(F_o)$] and 6.76% for all 553 independent reflections. As observed for the susannite structure (Steele et al. 1999) and for heated leadhillite, the absolute structure cannot be reliably determined. In fact, the Flack parameter is 0.48(8) for the data presented here, and 0.51(8) for the inverted structure. For their refinement of the susannite structure, Steele et al. (1999) used soft constraints for both SO₄ and CO₃ groups that allowed the S-O and C-O distances to vary but constrained the geometry of the SO₄ and CO₃ units to be tetrahedral and trigonal, respectively. The same soft constraints were used in this study.

RESULTS AND DISCUSSION

Unit-cell parameters

The variations of the unit-cell parameters for both the heating and cooling experiments are shown in Figure 1. It is clear that

TABLE 2A. Unit-cell parameters for leadhillite in the heating experiment from 25 to 100 °C

<i>T</i> (°C)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	<i>V</i> (Å ³)
25	9.104(2)	20.795(6)	11.577(3)	90.50(2)	2191.7(9)
32	9.104(3)	20.796(6)	11.578(4)	90.49(2)	2192(1)
35	9.103(3)	20.801(7)	11.578(4)	90.50(2)	2192(1)
37	9.103(3)	20.803(7)	11.579(4)	90.48(3)	2193(1)
40	9.102(4)	20.804(8)	11.579(4)	90.47(4)	2193(1)
42	9.102(4)	20.805(8)	11.579(5)	90.47(4)	2193(2)
45	9.102(4)	20.807(8)	11.580(5)	90.46(4)	2193(2)
48	9.101(4)	20.811(9)	11.581(5)	90.45(4)	2193(2)
50	9.100(4)	20.822(10)	11.581(5)	90.44(5)	2194(2)
53	9.097(5)	20.834(10)	11.583(6)	90.43(5)	2195(2)
56	9.095(5)	20.845(10)	11.586(6)	90.40(5)	2196(2)
59	9.094(5)	20.856(11)	11.589(7)	90.38(5)	2198(2)
62	9.092(5)	20.864(12)	11.593(7)	90.35(6)	2199(2)
65	9.088(6)	20.874(12)	11.597(8)	90.31(6)	2200(2)
68	9.084(7)	20.887(13)	11.602(8)	90.25(6)	2201(3)
71	9.080(7)	20.901(13)	11.605(8)	90.15(6)	2202(3)
75	9.078(8)	20.934(14)	11.608(9)	90.08(7)	2206(3)
79	9.077(8)	20.962(21)	11.611(9)	90.00(7)	2209(4)
82	9.077(8)		11.613(9)		829(1)
85	9.078(8)		11.614(9)		829(1)
90	9.077(8)		11.614(10)		829(1)
95	9.077(8)		11.615(10)		829(1)
100	9.077(9)		11.615(10)		829(1)

Note: The unit-cell parameters obtained at 82 °C for leadhillite can be transformed to those of susannite by the matrix [1 0 0, -1/2 3/8 0, 0 0 1]. They are *a* = 9.077(8) Å, *c* = 11.611(9) Å, *V* = 828(1) Å³.

TABLE 2B. Unit-cell parameters for leadhillite in the cooling experiment from 100 to 25 °C

<i>T</i> (°C)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	<i>V</i> (Å ³)
25	9.105(10)	20.790(23)	11.575(12)	90.53(11)	2191(4)
32	9.105(10)	20.794(22)	11.576(12)	90.52(11)	2192(4)
35	9.104(11)	20.795(22)	11.579(11)	90.54(11)	2192(4)
37	9.103(10)	20.800(21)	11.578(11)	90.52(10)	2192(4)
40	9.104(11)	20.805(21)	11.577(11)	90.51(10)	2193(4)
42	9.102(10)	20.804(20)	11.579(11)	90.49(10)	2193(4)
45	9.103(10)	20.802(19)	11.581(11)	90.47(10)	2193(4)
48	9.102(9)	20.808(19)	11.580(10)	90.48(9)	2193(4)
50	9.102(9)	20.808(18)	11.581(10)	90.45(9)	2193(3)
53	9.099(9)	20.819(18)	11.579(10)	90.45(9)	2193(3)
56	9.098(10)	20.832(18)	11.582(10)	90.40(9)	2195(4)
59	9.096(10)	20.848(18)	11.589(10)	90.38(9)	2198(4)
62	9.095(9)	20.853(17)	11.590(10)	90.34(9)	2198(3)
65	9.093(10)	20.862(17)	11.590(10)	90.33(8)	2199(4)
68	9.089(10)	20.875(17)	11.594(9)	90.34(8)	2200(3)
71	9.083(10)	20.883(16)	11.605(9)	90.26(8)	2201(3)
75	9.081(10)	20.907(16)	11.607(9)	90.11(8)	2204(3)
79	9.076(9)	20.930(16)	11.611(9)	90.05(7)	2206(3)
82	9.077(9)	20.963(18)	11.611(9)	90.00(6)	2209(4)
85	9.078(9)		11.613(10)		829(1)
90	9.077(9)		11.615(9)		829(1)
95	9.078(9)		11.615(9)		829(1)
100	9.078(9)		11.616(10)		829(1)

Note: The unit-cell parameters obtained at 82 °C for leadhillite can be transformed to those of susannite by the matrix [1 0 0, -1/2 3/8 0, 0 0 1]. They are *a* = 9.077(9) Å, *c* = 11.611(9) Å, *V* = 828(1) Å³.

the unit-cell parameters measured either with increasing or with decreasing temperature are in excellent agreement indicating that no hysteresis occurs within the temperature range examined and that the phase transformation is completely reversible in character. In detail, the *a* parameter slightly decreases when the temperature rises, whereas the *c* parameter slightly increases. The more enhanced *b* parameter strongly increases from 20.792(6) Å at room temperature to 20.962(21) Å at 82 °C. The β angle decreases when the temperature rises, reaching a value of 90.00(7)° at the transition temperature (82 °C).

According to Giuseppetti et al. (1990), the crystal structure of leadhillite shows a clear pseudo-trigonal subcell (*a* = 5.24, *b* =

5.21, $c = 11.59 \text{ \AA}$, $\alpha = 90$, $\beta = 90.40$, $\gamma = 119.76^\circ$) with a volume one-eighth that of the leadhillite unit cell. The transformation matrices that relate the subcell to leadhillite and susannite are $[2 \ 1 \ 0, 0 \ 4 \ 0, 0 \ 0 \ 1]$ and $[2 \ 1 \ 0, \bar{1} \ 1 \ 0, 0 \ 0 \ 1]$, respectively. The geometric relationships between the three unit cells are depicted in Figure 2. As shown in Figure 3, the displacive character of the phase transformation is shown by the variation of the unit-cell parameters of the pseudo-trigonal subcell present in leadhillite. At the transition temperature the a and b values of the subcell converge to a common value. This means that at 82°C the pseudo-trigonal subcell assumes trigonal symmetry.

Strain calculations and Landau theory

Following Carpenter et al. (1998) the strain calculations were done by a linear fit of the lattice parameters above 79°C and their extrapolation to room temperature. The components of the macroscopic spontaneous strain together with the scalar strain (ϵ_{ss}), calculated following Carpenter et al. (1998), are reported in Table 3 and plotted in Figure 4 as a function of temperature. It is worth noting that V_s does not show significant changes up

to 50°C . After this temperature V_s decreases up to the transition temperature that can be estimated to be about 82°C (Fig. 4). A similar behavior can be observed for the other components of the spontaneous strain. Therefore, one can argue that the crystal

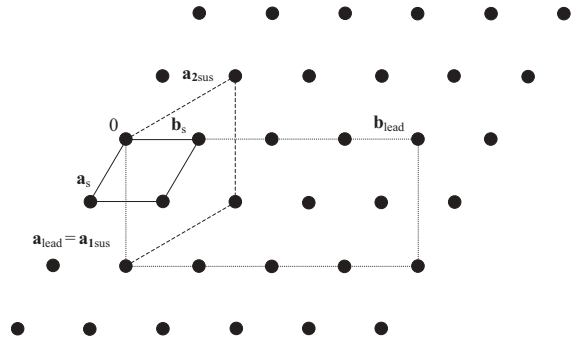


FIGURE 2. Geometric relationships between the pseudo-trigonal subcell (solid line), the leadhillite unit cell (dotted line), and the susannite unit cell (dashed line).

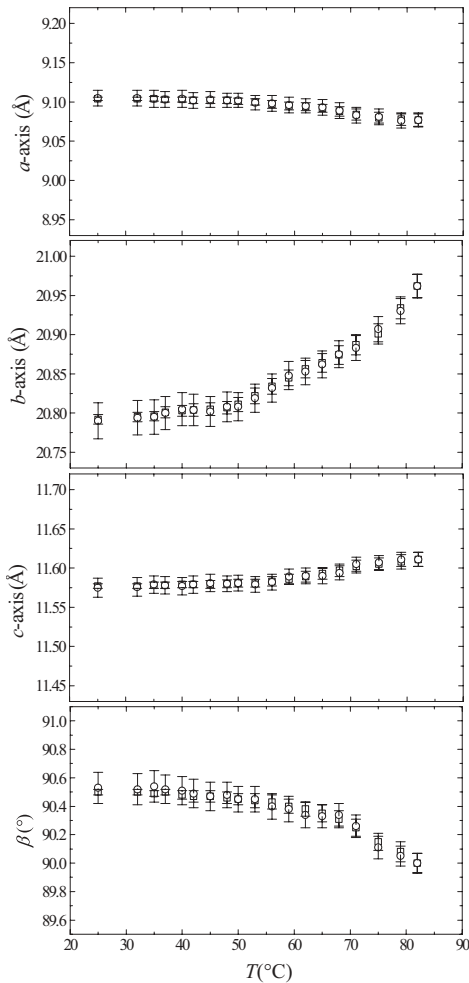


FIGURE 1. Variation of the unit-cell parameters with temperature. Squares refer to the values obtained in the heating experiment, circles to the values obtained in the cooling experiment.

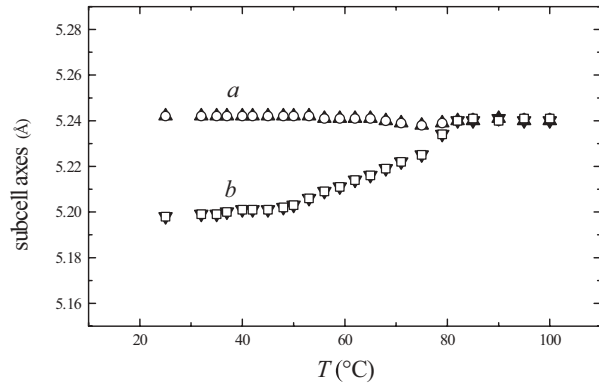


FIGURE 3. Variation of the axes of the pseudo-trigonal subcell with temperature. Filled up-pointing and down-pointing triangles refer to the values of a and b , respectively, in the heating experiment. Open circles and squares refer to the values of a and b , respectively, in the cooling experiment.

TABLE 3. Principal axes ($\times 10^{-3}$) of the strain ellipsoid, scalar strain ($\times 10^{-3}$), and the ordering parameter (Σ_l/Σ_l) measured for leadhillite in the heating experiment

T ($^\circ\text{C}$)	e_{11}	e_{22}	e_{33}	e_{13}	ϵ_{ss}	V_s	Σ_l/Σ_l
25	2.9	-8.2	-2.1	-4.4	12.5	-6.4	0.267
32	2.9	-8.0	-2.2	-4.4	12.4	-6.4	0.272
35	2.9	-8.0	-2.2	-4.3	12.2	-6.4	0.274
37	2.8	-7.7	-2.2	-4.4	12.2	-6.4	0.274
40	2.8	-7.6	-2.1	-4.2	11.9	-6.0	0.273
42	2.7	-7.6	-2.2	-4.1	11.7	-6.1	0.267
45	2.7	-7.5	-2.2	-4.1	11.7	-6.2	0.260
48	2.7	-7.4	-2.2	-4.0	11.5	-6.3	0.255
50	2.6	-7.2	-2.1	-3.9	11.2	-6.3	0.251
53	2.5	-6.7	-2.2	-3.8	10.7	-6.0	0.239
56	2.2	-6.1	-2.1	-3.7	10.1	-5.6	0.223
59	2.0	-5.6	-1.9	-3.5	9.3	-5.2	0.206
62	1.8	-5.1	-1.6	-3.3	8.7	-4.4	0.182
65	1.6	-4.7	-1.3	-3.1	8.0	-4.1	0.146
68	1.2	-4.2	-1.0	-2.7	7.0	-3.7	0.122
71	0.7	-3.6	-0.7	-2.2	5.7	-3.3	0.082
75	0.3	-2.9	-0.5	-1.3	4.0	-3.0	0.047
79	0.1	-1.4	-0.3	-0.7	2.0	-1.3	0.026
82	0.0	0.0	-0.1	0.0	0.1	0.0	0.004

structure of leadhillite exhibits only normal thermal expansion up to 50 °C and that the structural distortions leading to the topology of heated leadhillite take place in the temperature range 50–82 °C.

As it is well known, Landau theory is commonly used to describe displacive phase transitions (Dove and Redfern 1997, and references therein). A proper Landau expansion in one order parameter with second, fourth, and sixth order terms (246 potential)

$$G = \frac{1}{2}a_D(T - T_c)Q_D^2 + \frac{1}{4}b_DQ_D^4 + \frac{1}{6}c_DQ_D^6 \quad (1)$$

where a , b , and c are Landau coefficients and Q_D is the order parameter, can be used to derive the dependence of Q_D^2 on T . A simpler 24 Landau potential can also be used:

$$G = \frac{1}{2}a_D(T - T_c)Q_D^2 + \frac{1}{4}b_DQ_D^4 \quad (2)$$

According to Carpenter et al. (1998) the order parameter Q_D is proportional to the aggregate intensity ratio, $\Sigma I_S/\Sigma I$, where I_S are the intensities of the reflections that are present only in the room-temperature crystal structure (leadhillite), and I the intensities of the reflections that are always present in both the room- and high-temperature structures. For this purpose, we monitored the intensities of the 232 and 250 reflections in the leadhillite monoclinic setting (S-type), and of reflections 202 and 404, which are always present. Both the character of the phase transition and the T_c value can be obtained following the evolution of $\Sigma I_S/\Sigma I$ as a function of temperature. Our data show that $\Sigma I_S/\Sigma I$ decreases continuously from room T to ~82 °C (Fig. 5). Beyond this value, S-type reflections are no longer detectable, and the crystal shows $P3$ symmetry. If we assume a 246 Landau potential taking in mind that repeated heating and cooling cycles showed the same behavior (no hysteresis was detected), we obtain $Q_D^2 \propto \Sigma I_S/\Sigma I$. By substitution in Equation 1, we can calculate T_c from the measured evolution of S-type reflections from a polynomial fit of:

$$T = T_c + \frac{b_D}{a_D}(\Sigma I_S/\Sigma I) + \frac{c_D}{a_D}(\Sigma I_S/\Sigma I)^2 \quad (3)$$

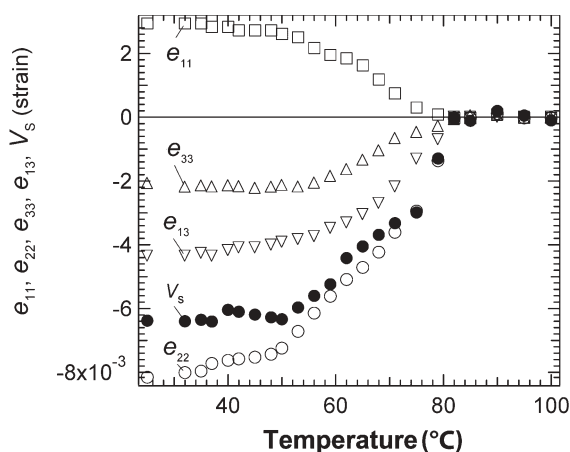


FIGURE 4. Variation of the components of the strain tensors and of the strain volume as a function of temperature.

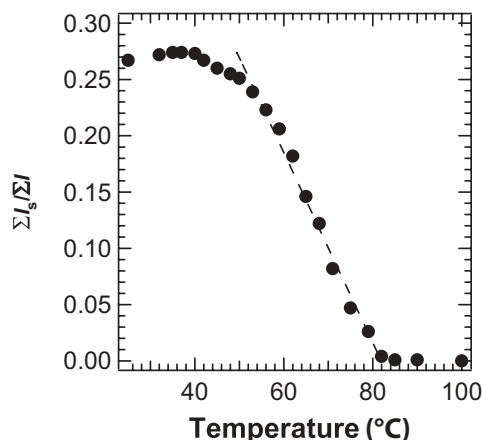


FIGURE 5. Variation of the aggregate intensity ratio between the intensities of the reflections that are present only in the room-temperature crystal structure, and the intensities of the reflections that are always present in both the room- and high-temperature. The dashed line represents the linear fit to the experimental data in terms of a 24 Landau expansion.

As the structure does not show any change in the volume strain up to 50 °C we did not fit data at $T < 50$ °C (see strain section). The data measured in the T range 50–80 °C gave a calculated T_c of 81(1) °C. However, since $c_D/a_D \equiv \sigma(c_D/a_D)$ it would be better to use a simplified 24 Landau treatment. Hence T_c can be obtained by a linear fit of:

$$T = T_c + \frac{b_D}{a_D}(\Sigma I_S/\Sigma I) \quad (4)$$

which yielded $T_c = 81.9(7)$ °C and $b_D/a_D = -118(4)$ °C. This result is in excellent agreement with the value of 81 °C deduced from the DSC measurements (Milodowski and Morgan 1984).

The present results are compatible with a second-order character for the $P2_1/a \leftrightarrow P3$ phase transition in leadhillite.

Crystal structure of leadhillite

Fractional atomic coordinates and isotropic displacement parameters are given in Table 4. Table 5¹ reports the anisotropic displacement parameters. Table 6 reports bond distances. For clarity we used the same labels as Giuseppetti et al. (1990).

On the whole, the crystal structure of leadhillite refined here is topologically identical to that reported by Giuseppetti et al. (1990), although a much higher precision was attained in the present refinement. According to Steele et al. (1998, 1999), the structure of leadhillite can be described as being composed of three different kinds of layers (A = sulfate; B = Pb; C = carbonate)

¹ Deposit item AM-05-024, Table 5. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at <http://www.minsocam.org>, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

parallel to (001). The stacking sequence of the layers is ...ABC-CBABCCB... The mean Pb-O distances for the eight Pb atoms as well as the bond lengths in the SO₄ tetrahedra and CO₃ triangles are in agreement with those found by Giuseppetti et al. (1990). In spite of the high-quality of the diffraction data, however, we were not able to locate the hydrogen positions from the difference Fourier maps. An electrostatic valence balance was calculated according to the method of Brown and Altermatt (1985) for all oxygen atoms. The bond-strength sums for OHa, OHb, OHc, and OHd (1.52, 1.35, 1.33, and 1.22 v.u., respectively), supports the hypothesis proposed by Giuseppetti et al. (1990) that these oxygen atoms act as donors in hydrogen bonding.

Crystal structure of heated leadhillite (susannite)

Fractional atomic coordinates and equivalent isotropic displacement parameters are given in Table 7. Table 8 reports the bond distances. As described in the experimental section, we used the same labels as Steele et al. (1999). In detail, we found that the crystal structure of heated leadhillite exhibits the same sequence of layers as observed in leadhillite (i.e., ...ABC-CBABCCB...). As in susannite (Steele et al. 1999), the Pb1 and Pb2 atoms coordinate six nearly coplanar oxygen atoms parallel to (001) and one OH group [i.e., O1 and O2, respectively] above or below the adjacent B layer. The average distances for Pb1 and Pb2 atoms in heated leadhillite for the six planar oxygen atoms are 2.67 and 2.71 Å, respectively; these values are in

close agreement with those (2.665 and 2.685 Å) reported by Steele et al. (1999) for the crystal structure of susannite. On the other hand, some differences are found for Pb3 and Pb4 atoms. For example, the Pb3-O2 distance in susannite (Steele et al. 1999) is markedly shorter than that found in heated leadhillite. However, the value obtained in this study could be influenced by poorer data. In heated leadhillite, the double carbonate layer can be considered a rigid unit and it is topologically identical to that observed for the other trimorphs (Giuseppetti et al. 1990; Steele et al. 1998, 1999).

Comparison between leadhillite and heated leadhillite (susannite)

Figure 6 shows a comparison between layer A (sulfate groups) of the heated leadhillite refined here and layer A of susannite

TABLE 4. Fractional atomic coordinates and equivalent isotropic displacement parameters for leadhillite at room temperature

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Pb1a	0.41786(3)	0.17889(1)	0.10828(2)	0.02532(7)
Pb1b	0.42953(3)	0.43245(1)	0.10341(3)	0.02627(7)
Pb1c	0.41429(3)	0.69339(1)	0.09389(3)	0.02514(7)
Pb1d	0.40651(3)	0.93851(1)	0.10321(3)	0.02416(7)
Pb2a	0.62598(3)	0.04793(1)	0.32112(2)	0.02337(7)
Pb2b	0.55846(3)	0.28260(1)	0.33797(2)	0.02450(7)
Pb2c	0.53538(3)	0.57362(1)	0.31877(3)	0.02629(7)
Pb2d	0.60782(3)	0.83185(1)	0.31875(3)	0.02696(7)
Sa	0.2297(3)	0.0737(1)	0.4879(2)	0.0430(5)
Sb	0.2385(3)	0.3175(1)	0.5132(2)	0.0458(6)
Ca	0.2550(8)	0.0577(3)	0.1583(6)	0.019(1)
Cb	0.2574(8)	0.3127(3)	0.1461(7)	0.022(1)
Cc	0.2513(9)	0.5632(3)	0.1235(7)	0.020(1)
Cd	0.2490(8)	0.8098(3)	0.1565(6)	0.018(1)
O1a	0.0733(9)	0.0868(4)	0.4662(6)	0.056(2)
O1b	0.1004(9)	0.2811(4)	0.5416(6)	0.056(2)
O2a	0.3001(8)	0.1378(3)	0.4754(6)	0.047(2)
O2b	0.2084(8)	0.3866(3)	0.5109(6)	0.049(2)
O3a	0.2844(9)	0.0248(4)	0.4110(6)	0.055(2)
O3b	0.2915(8)	0.2927(3)	0.3989(6)	0.049(2)
O4a	0.2413(9)	0.0550(3)	0.6143(6)	0.050(2)
O4b	0.3451(8)	0.3045(3)	0.6065(6)	0.050(2)
O5a	0.1851(9)	0.0049(4)	0.1507(6)	0.053(2)
O5b	0.1835(9)	0.2583(5)	0.1524(6)	0.060(2)
O5c	0.1832(8)	0.5083(4)	0.1304(5)	0.046(2)
O5d	0.1725(9)	0.7581(4)	0.1384(6)	0.055(2)
O6a	0.3947(9)	0.0564(4)	0.1505(7)	0.059(2)
O6b	0.4009(9)	0.3103(4)	0.1474(7)	0.061(2)
O6c	0.3945(9)	0.5621(3)	0.1242(7)	0.052(2)
O6d	0.3861(9)	0.8061(4)	0.1498(7)	0.059(2)
O7a	0.1826(9)	0.1137(4)	0.1636(6)	0.056(2)
O7b	0.1839(9)	0.3664(4)	0.1323(6)	0.056(2)
O7c	0.1728(8)	0.6160(4)	0.1187(6)	0.049(2)
O7d	0.1813(9)	0.8672(4)	0.1512(6)	0.051(2)
OHa	0.4663(8)	0.1840(4)	0.2936(6)	0.054(2)
OHb	0.3858(9)	0.4481(3)	0.2877(6)	0.052(2)
OHc	0.3865(8)	0.6714(3)	0.2837(6)	0.047(2)
OHd	0.4692(8)	0.9354(3)	0.2905(6)	0.048(2)

TABLE 6. Bond distances (Å) for leadhillite

Pb1a - OHa	2.189(7)	Pb1b - OHb	2.198(7)
- O6a	2.602(7)	- O7a	2.586(8)
- O7b	2.611(8)	- O6b	2.604(8)
- O7a	2.619(8)	- O7b	2.648(8)
- O5b	2.749(9)	- O5a	2.718(8)
- O6b	2.774(9)	- O6c	2.725(6)
- O5b	2.792(9)	- O5c	2.762(8)
- O7c	3.043(9)	- O6c	3.098(8)
- O5d	3.392(10)	- O7d	3.390(9)
- O6d	3.508(10)	- O5a	3.458(9)
Pb1c - OHc	2.261(6)	Pb1d - OHd	2.238(7)
- O6d	2.445(8)	- O5a	2.508(8)
- O5d	2.605(8)	- O6a	2.514(7)
- O5d	2.635(8)	- O7d	2.594(8)
- O7c	2.742(7)	- O7c	2.681(7)
- O6c	2.758(6)	- O5c	2.767(7)
- O7d	2.812(8)	- O6d	2.812(8)
- O5b	3.271(8)	- O5c	3.170(8)
- O6b	3.274(9)	- O7b	3.212(9)
- O7a	3.516(9)	- O6a	3.465(10)
Pb2a - OHb	2.402(8)	Pb2b - OHa	2.272(8)
- O5c	2.556(7)	- O3b	2.545(7)
- O4a	2.566(7)	- O5b	2.584(8)
- O2b	2.686(7)	- O6b	2.684(8)
- OHd	2.762(8)	- O3b	2.725(7)
- O7b	2.872(8)	- O1b	2.728(7)
- O6a	2.880(8)	- O1a	3.097(8)
- OHa	3.195(9)	- O7a	3.169(8)
- O3a	3.323(10)	- O2a	3.170(9)
- O3a	3.539(10)		
Pb2c - OHc	2.475(7)	Pb2d - OHd	2.516(7)
- O6c	2.593(7)	- OHc	2.574(7)
- O7d	2.662(7)	- O2a	2.597(7)
- O4a	2.670(8)	- O7c	2.629(7)
- O1a	2.701(7)	- O1b	2.716(7)
- O4b	2.888(8)	- O4a	2.829(7)
- O5a	2.891(8)	- O6d	2.849(8)
- OHb	2.964(8)	- O5d	2.868(8)
- O2b	3.152(9)	- O4b	2.994(8)
- O3a	3.229(10)		
Sa - O3a	1.443(8)	Sb - O2b	1.463(7)
- O1a	1.469(8)	- O4b	1.471(7)
- O2a	1.486(7)	- O3b	1.504(8)
- O4a	1.517(8)	- O1b	1.506(7)
Ca - O5a	1.272(10)	Cb - O6b	1.307(11)
- O6a	1.276(11)	- O7b	1.311(11)
- O7a	1.340(10)	- O5b	1.318(11)
Cc - O5c	1.302(11)	Cd - O6d	1.254(10)
- O6c	1.304(9)	- O5d	1.297(10)
- O7c	1.311(10)	- O7d	1.344(10)

(Steele et al. 1999). Following Steele et al. (1998), we used the notations “U” and “D” to refer to up-pointing and down-pointing tetrahedra, respectively. It is clearly evident that the orientations of the sulfate tetrahedra are identical. We found the repeat pattern ...UUDUUD... in the direction of \mathbf{a}^* (Fig. 6). On the other hand, for leadhillite a row of sulfate tetrahedra parallel to [010] (which equates the direction of \mathbf{a}^* of susannite) shows the sequence ...UDDUDDU... (Fig. 7).

The structural features outlined above strongly support the assumption of Steele et al. (1999) that the reversible phase transformation between leadhillite and heated leadhillite (susannite) requires a reorientation of two sulfate groups within four su-

sannite unit cells. In particular the up-pointing Sb tetrahedron in leadhillite changes its orientation to the down-pointing $S2$ tetrahedron in heated leadhillite at the transition temperature. In detail, the $O4b$ of leadhillite becomes $O11$ of heated leadhillite and $O1b$, $O2b$, and $O3b$ of leadhillite become the three equivalent $O12$ atoms of heated leadhillite. However, as pointed out by Steele et al. (1999) for the crystal structure of susannite, the change in the tetrahedral orientation is compensated by changes in the Pb-O coordination within the B layer. For example, the bond distance $Pb2a-O3a$ in the leadhillite structure [3.323(10) Å] strongly decreases to 2.76(8) Å in heated leadhillite [Pb4-O14 bond distance].

TABLE 7. Fractional atomic coordinates and isotropic displacement parameters for heated leadhillite

	x	y	z	U_{iso}
Pb1	0.6677(5)	0.9881(5)	0.020(1)	0.038(1)
Pb2	0.3481(5)	0.0136(5)	0.816(1)	0.036(1)
Pb3	0.6710(5)	0.9458(5)	0.592(1)	0.036(1)
Pb4	0.6607(5)	0.6117(6)	0.241(1)	0.035(1)
S1	2/3	1/3	0.43(1)	0.042(2)
S2	1/3	2/3	0.41(2)	0.051(2)
S3	0	0	0.41(1)	0.051(3)
C1	0	0	0.07(2)	0.029(2)
C2	1/3	2/3	0.07(1)	0.031(2)
C3	2/3	1/3	0.05(1)	0.031(2)
C4	1/3	2/3	0.78(1)	0.031(2)
C5	0	0	0.78(1)	0.030(3)
C6	2/3	1/3	0.76(2)	0.029(3)
O1	0.66(1)	0.03(1)	0.214(7)	0.056(4)
O2	0.36(1)	0.03(1)	0.607(8)	0.05(3)
O3	0.86(1)	-0.14(1)	0.06(1)	0.065(2)
O4	0.47(1)	-0.32(1)	0.06(1)	0.068(3)
O5	0.66(1)	0.47(1)	0.04(1)	0.068(2)
O6	0.48(1)	-0.19(2)	0.77(1)	0.060(3)
O7	-0.002(9)	-0.14(1)	0.77(1)	0.061(3)
O8	0.52(1)	0.33(1)	0.75(1)	0.064(3)
O9	2/3	1/3	0.31(1)	0.053(2)
O10	0.83(2)	0.38(2)	0.46(1)	0.050(2)
O11	1/3	2/3	0.53(2)	0.062(3)
O12	0.51(1)	0.76(1)	0.37(1)	0.063(3)
O13	0	0	0.53(1)	0.069(3)
O14	0.17(1)	0.111(1)	0.37(1)	0.061(2)

TABLE 8. Bond distances (Å) for heated leadhillite

Pb1 - O1	2.29(8)	Pb2 - O2	2.43(8)
- O4	2.50(7)	- O8	2.61(8)
- O3	2.6(1)	- O8	2.65(8)
- O3	2.66(8)	- O7	2.7(1)
- O5	2.7(1)	- O6	2.7(1)
- O4	2.78(8)	- O6	2.8(2)
- O5	2.79(8)	- O7	2.8(2)
		- O5	3.1(1)
Pb3 - O6	2.6(1)	Pb4 - O1	2.58(6)
- O7	2.6(1)	- O5	2.66(6)
- O2	2.78(6)	- O9	2.68(4)
- O13	2.87(3)	- O1	2.75(9)
- O8	2.9(1)	- O14	2.76(8)
- O11	2.93(6)	- O10	2.9(1)
- O12	3.0(1)	- O12	2.9(2)
- O14	3.1(1)	- O3	2.95(9)
- O10	3.2(2)	- O4	3.0(1)
S1 - O9	1.4(2)	S2 - O11	1.4(2)
- O10 (x3)	1.4(1)	- O12 (x3)	1.4(1)
S3 - O13	1.4(2)		
- O14 (x3)	1.43(7)		
C5 - O7 (x3)	1.27(7)	C2 - O4 (x3)	1.2(1)
C3 - O5 (x3)	1.28(7)	C4 - O6 (x3)	1.3(1)
C1 - O3 (x3)	1.3(1)	C6 - O8 (x3)	1.32(7)

CONCLUDING STATEMENTS

Our study confirms that the crystal structure of heated leadhillite is very close to that of susannite. We demonstrate by means of an in situ data collection at 82 °C that the slight structural changes occurring during the phase transformation are mainly restricted to the sulfate sheets. The double carbonate layer, indeed, is a constant rigid unit in all three structures of the trimorphs (Giuseppetti et al. 1990; Steele et al. 1998, 1999). A change in the sequence of up or down pointing SO_4 tetrahedra occurs within the temperature range. However, on the basis of the variation of the unit cell parameters, one can speculate that a sudden structural change is rather unlikely. Steele et al. (1999) suggested that in the phase transformation some bonds had to be broken although without major reorientation because of the reversible nature of

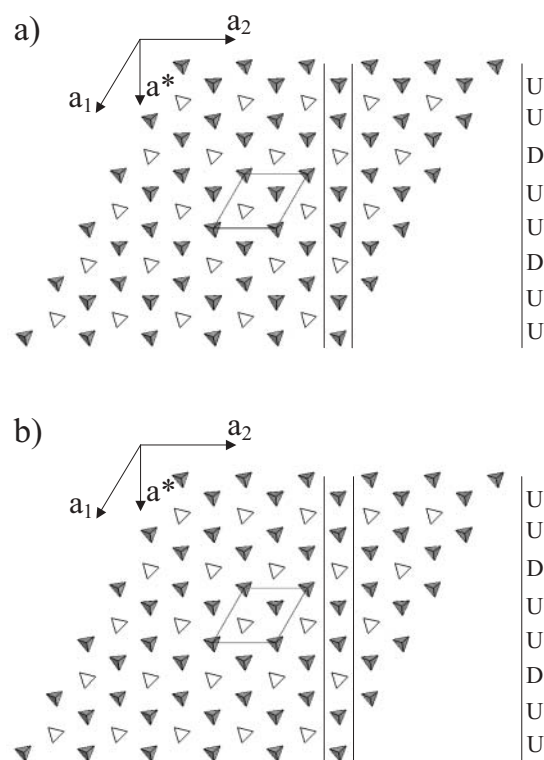


FIGURE 6. Comparison of sulfate tetrahedra in the heated leadhillite structure [(a) this study] and in susannite [(b) Steele et al. 1999]. U and D indicate up and down pointing sulfate tetrahedra, respectively. The unit cells are outlined.

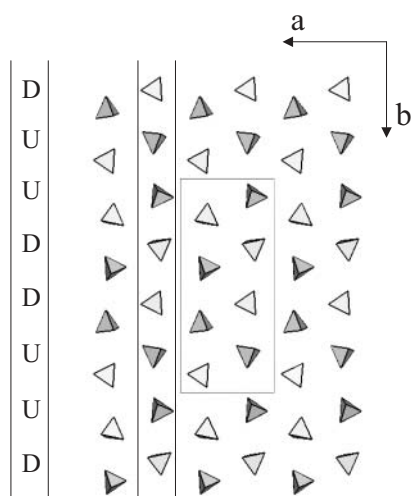


FIGURE 7. Sulfate tetrahedra (A layer) of the leadhillite structure (this study). U and D indicate up and down pointing sulfate tetrahedra, respectively. The unit cell is outlined.

the transition. By means of analysis of the components of the spontaneous strain we determined that the crystal structure of leadhillite shows only normal thermal expansion up to 50 °C and that the structural distortions leading to the topology of heated leadhillite take place in the temperature range 50–82 °C. After 50 °C, indeed, some Pb-O bonds (with oxygen atoms of the sulfate tetrahedra) break thus causing rotation of the sulfate tetrahedra. The rotation goes on until a ...UUDUUD... stable configuration is obtained. However, the changes in the orientation of sulfate tetrahedra and in the Pb-O coordination polyhedra occur in a continuous way within the temperature range investigated as indicated by the second-order character of the phase transition. In this way, the leadhillite structure gradually goes toward that of susannite without abrupt structural changes.

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