

The Precision of Thermal-Expansion Tensors of Triclinic and Monoclinic Crystals

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Abstract

If thermal-expansion-tensor components α_{ij} are determined from temperature-induced changes in d values, most authors first calculate the unit-cell parameters at different temperatures. From these, the α_{ij} are computed. It is shown that this procedure involves a reduced precision if compared with the direct least-squares determination of α_{ij} from changes in the d values.

Introduction

The experimental method used to determine the thermal expansion of crystals depends on the size of the specimens available. If large crystals (several millimetres in size) can be obtained, interferometric methods or path-sensitive detectors are usually employed. If only small crystals are available, X-ray methods are used to measure the changes in d values, Δd , produced by changes in temperature, ΔT . Thermal expansion is represented by a second-rank tensor, $[\alpha_{ij}]$. Therefore, the number of tensor components and, consequently, the number of independent measurements that are necessary to determine $[\alpha_{ij}]$ and the directions of the principal axes, depends on the crystal symmetry. In the tetragonal, trigonal, hexagonal and orthorhombic systems, the principal axes of the α tensor are parallel to the crystallographic axes. Therefore, the relative changes in the unit-cell parameters immediately yield the principal components of $[\alpha_{ij}]$. In the triclinic system, however, the principal axes are not related to any crystallographic axes. If at least six independent $\Delta d/(d\Delta T)$ values of reflections with Miller indices $(h_m k_m l_m)$ have been measured, the six components of the (symmetric) $[\alpha_{ij}]$ tensor can be easily determined from the six equations ($m = 1, 6$)

$$\alpha'_m = [\Delta d/(d\Delta T)]_m = \sum_i \sum_j a_{mi} a_{mj} \alpha_{ij}, \quad (1)$$

with a_{mk} being the direction cosines of a vector pointing normal to the m th reflecting lattice plane, with respect to the axes of a given Cartesian system $\{\mathbf{e}_k\}$ ($i, j, k = 1, 2, 3$). If more than six independent

measurements have been performed, least-squares methods are applied to obtain the 'best' set of α_{ij} to fit the measured data. This method for the direct determination of α_{ij} , which has been described for instance by Haussühl (1983), will be termed method I in the following discussion.

In the monoclinic system, one principal axis of $[\alpha_{ij}]$ is parallel to the unique crystallographic axis which is usually termed b . Therefore, one principal component, α_{22} , is given directly by the relative change in the b axis; the other two principal axes, however, have no relation to the crystallographic axes a and c . The remaining α_{ij} (α_{11} , α_{33} , α_{13}) can be determined similarly as for the case of the triclinic system by a least-squares procedure.

In spite of the lack of relation to the crystallographic axes, in the vast majority of studies dealing with the X-ray determination of the components of the α tensor of triclinic or monoclinic crystals, authors calculate first the thermal expansion of the unit cell, *i.e.* the relative changes of the three edges and the three angles of the unit cell. Then, in a subsequent computational step, the $[\alpha_{ij}]$ tensor (related to a given Cartesian system) is calculated by the application of certain complicated formulae (*e.g.* those presented by Schlenker, Gibbs & Boisen, 1978). This means that the thermal expansion is referred intermediately to the oblique crystallographic system, which is then abandoned in favour of the finally chosen Cartesian system. This second procedure for the determination of α values will be termed method II below.

The present paper demonstrates that method II is an indirect and nonoptimal procedure because it introduces superfluous calculations which decrease the precision of the final results through a propagation of errors. In the case that both the thermal-expansion tensor and the temperature behaviour of the unit cell are of interest, it is recommended that both should be computed separately starting with the original experimental data ($\Delta d_m/d_m \Delta T$). A review of the literature revealed eight papers that dealt with the X-ray determination of the thermal-expansion tensors of triclinic crystals and 35 papers concerning monoclinic crystals (the list of these citations has

been deposited,[†] or can be obtained from the authors). Method I was applied to only one triclinic and to 15 of the monoclinic crystals. The other examples were calculated using the less-recommended method II.

Fig. 1 is a flow chart of the essential steps of the two methods. In both cases, the primary data consist of a set of measured Bragg angles θ_{hkl} (or d values d_{hkl}) of several ($N \geq 6$) hkl reflections obtained at different temperatures T_n . The Cartesian reference system $\{e_1, e_2, e_3\}$ is chosen according to the IRE (Institution of Radio Engineers) convention: $e_3 \parallel c$, $e_2 \parallel b^*$, $e_1 = e_2 \times e_3$ (cf., for example, Haussühl, 1983).

Method I

For each of the N reflections, the measured thermal expansions α'_m ($m = 1, \dots, N$) are along the directions perpendicular to the corresponding lattice planes (i.e. parallel to $h_m = h_m a^* + k_m b^* + l_m c^*$). The appropriate direction cosines are (Haussühl, 1983)

$$a_{m1} = (h_m c - l_m a \cos \beta) / V b^* |h_m|; \quad a_{m3} = l_m / c |h_m|;$$

$$a_{m2} = (h_m a^* \cos \gamma^* + k_m b^* + l_m c^* \cos \alpha^*) / |h_m|.$$

[†] A list of publications determining thermal-expansion tensors by X-rays has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53806 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

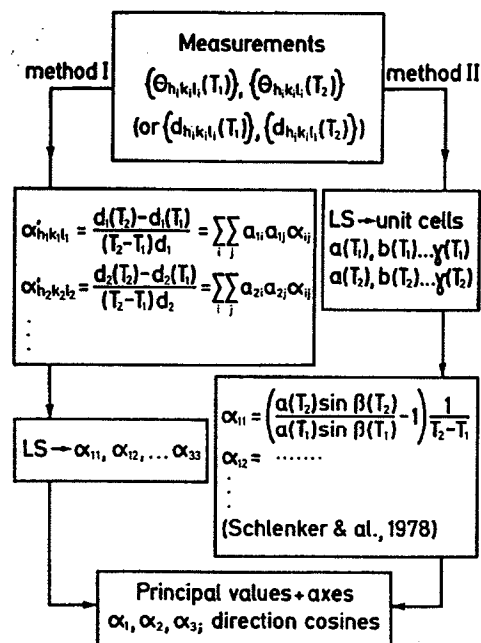


Fig. 1. Flow diagram of the evaluation of a set of θ values, measured at two temperatures T_1 and T_2 according to methods I and II. LS means least-squares procedures.

Table 1. Bragg angles ($^\circ$) of 19 reflections hkl of LHPM at six different temperatures

-h	k	l	T(K)					
			90.0	140.0	190.0	240.0	290.0	340.0
10	5	1	46.200	45.923	45.628	45.326	45.029	44.740
-4	-9	1	45.680	45.652	45.609	45.548	45.459	45.335
11	-6	1	47.198	47.166	47.134	47.086	47.062	47.024
10	-7	2	48.053	48.064	48.078	48.083	48.098	48.094
-13	4	2	49.869	49.728	49.589	49.446	49.319	49.206
1	9	3	48.127	48.175	48.216	48.253	48.271	48.281
-9	-7	3	48.788	48.580	48.341	48.074	47.790	47.505
9	-6	4	46.459	46.435	46.400	46.369	46.332	46.290
-1	-9	4	45.360	45.424	45.458	45.467	45.439	45.368
7	5	5	48.672	48.476	48.270	48.079	47.897	47.731
2	7	5	46.782	46.753	46.735	46.711	46.687	46.657
-10	-4	5	46.543	46.331	46.082	45.810	45.529	45.241
-8	5	6	48.019	48.034	48.053	48.070	48.084	48.095
4	-7	6	45.622	45.672	45.698	45.708	45.698	45.661
-7	-6	7	50.314	50.189	50.033	49.840	49.632	49.383
-1	6	7	49.791	49.803	49.815	49.831	49.842	49.854
1	-5	8	46.661	46.634	46.595	46.539	46.469	46.375
-3	-3	9	49.058	48.993	48.913	48.820	48.704	48.579
-3	1	9	49.250	49.201	49.147	49.083	49.023	48.959

Table 2. Tensor components of thermal expansion ($10^{-6} K^{-1}$) of LHPM as calculated by method I

Standard deviations given in parentheses in this and the following tables refer to the last significant digit.

T (K)	α_{11}	α_{22}	α_{33}	α_{23}	α_{13}	α_{12}
90-140	108(2)	-41(1)	24(1)	2.4(9)	3(1)	63(1)
140-190	114.1(9)	-36.6(8)	27.7(7)	-4.6(5)	1.5(7)	67.9(6)
190-240	117(1)	-29(1)	30.8(9)	-10.6(6)	-4.1(9)	68.2(7)
240-290	109(1)	-18(1)	33.7(9)	-16.5(6)	-6.9(9)	69.0(7)
290-340	102(1)	-3(1)	37(1)	-24.6(8)	-10(1)	65.2(9)

According to (1), an overdetermined system of N equations with the six unknown thermal-expansion-tensor components α_{11} , α_{22} , α_{33} , α_{23} , α_{31} and α_{12} results, which can be solved by least-squares methods. Thereafter, the tensor can be transformed to its principal axes.

Method II

In the first step (Fig. 1) the lattice constants at each temperature are determined by least-squares methods. The transformation of the unit-cell parameters, at the different temperatures, to the components α_{ij} is performed using formulae given by Schlenker *et al.* (1978). It should be noted that these authors claim to give their formulae for a Cartesian system as defined by the IRE convention; however, a different reference system was used ($e_3 \parallel c$, $e_1 \parallel a^*$, $e_2 = e_3 \times e_1$). The correct formulae, referring to the IRE system, can be derived from those given by Schlenker *et al.* (1978) by the following formal interchange: $x \leftrightarrow y$, $a \leftrightarrow b$ and $\alpha \leftrightarrow \beta$. The last step, the transformation to principal axes, is the same as for method I.

Table 3. *Lattice constants (\AA , °) of LHPM at six different temperatures*

T (K)	a	b	c	α	β	γ
90.0	11.663 (3)	8.948 (3)	7.899 (2)	96.89 (2)	95.86 (3)	94.55 (2)
140.0	11.726 (3)	8.926 (2)	7.908 (2)	96.90 (2)	95.82 (2)	94.24 (2)
190.0	11.792 (3)	8.906 (2)	7.919 (2)	96.95 (2)	95.79 (2)	93.90 (2)
240.0	11.862 (3)	8.890 (2)	7.932 (2)	97.04 (2)	95.79 (2)	93.54 (2)
290.0	11.927 (3)	8.881 (2)	7.945 (2)	97.15 (2)	95.81 (2)	93.16 (2)
340.0	11.989 (3)	8.878 (2)	7.960 (2)	97.30 (2)	95.84 (3)	92.80 (2)

Experimental examples

In order to illustrate the two different data-evaluation methods and the different development of errors, measurements of two triclinic crystals were performed: (a) lithium hydrogen phthalate monohydrate (LHPM), $\text{LiH}(\text{C}_8\text{H}_4\text{O}_4) \cdot \text{H}_2\text{O}$, and (b) potassium trihydrogen dioxalate dihydrate (PTOD), $\text{KH}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, which was formerly named 'potassium tetraoxalate dihydrate'. The structures of these two crystal species were determined by Küppers (1978) and Haas (1964), respectively. For unfortunate technical reasons, only Mo $K\alpha$ radiation was available. Therefore, the accessible θ diffraction space was limited to angles of $2\theta < 50^\circ$. Greater accuracy and precision could have been obtained from reflections with larger θ angles if Cu $K\alpha$ radiation had been used. Nevertheless, the present measurements illustrate our arguments adequately.

The Bragg angles were measured with a four-circle diffractometer (AED2, Stoe-Siemens) equipped with a liquid-nitrogen cooling system (Oxford Cryosystem). The temperature uncertainty was ± 0.1 K. The reflections were scanned at positive and negative θ angles.

(a) LHPM

The measurements (Table 1) were performed at six different temperatures on a single-crystal specimen of LHPM with a mean diameter of approximately 1.0 mm and were carried out at the Stoe laboratory in Darmstadt. The results of the evaluation using method I are given in Table 2.

If the data are evaluated by method II, first, for different temperatures, the lattice constants with their e.s.d.'s are calculated (Table 3). The tensor components α_{ij} and their errors, which result from the use of the formulae of Schlenker *et al.* (1978), are given in Table 4. Comparison of Tables 2 and 4 shows that the precision of the results obtained from method II is appreciably less, by a factor of approximately seven.

(b) PTOD

These measurements were carried out at the Mineralogical Institute of the University of Kiel using a single-crystal specimen with a mean diameter

Table 4. *Tensor components of thermal expansion (10^{-6} K^{-1}) of LHPM as calculated by method II*

T (K)	α_{11}	α_{22}	α_{33}	α_{23}	α_{13}	α_{12}
90–140	109 (7)	−40 (8)	23 (7)	3 (5)	3 (6)	63 (5)
140–190	114 (7)	−37 (7)	28 (7)	−4 (5)	1 (5)	67 (5)
190–240	119 (7)	−30 (7)	33 (7)	−12 (5)	−4 (5)	68 (5)
240–290	109 (7)	−16 (7)	33 (7)	−17 (5)	−7 (5)	70 (5)
290–340	103 (7)	−5 (7)	38 (7)	−24 (5)	−9 (6)	64 (5)

Table 5. *Bragg angles ($^\circ$) of 19 reflections hkl of PTOD at two different temperatures*

			T (K)	
h	k	l	283.0	320.0
−1	−9	−6	49.287	49.273
4	7	−6	49.040	48.866
7	−1	−3	48.857	48.699
−4	8	−1	48.200	48.163
3	10	−4	48.234	48.088
−6	−8	−1	47.639	47.506
6	−4	−1	46.333	46.255
1	11	−2	46.148	46.064
−1	8	−4	44.743	44.708
3	3	−7	45.196	45.080
−5	−1	−4	44.826	44.801
−4	3	−4	43.980	43.971
−2	−9	−5	46.399	46.376
−2	6	−5	46.428	46.418
7	2	−4	48.968	48.758
7	2	−2	46.269	46.097
7	4	0	47.245	47.100
0	5	−7	49.165	49.112
1	0	−8	47.868	47.812

Table 6. *Tensor components of thermal expansion (10^{-6} K^{-1}) of PTOD as calculated by method I (upper row) and method II (lower row)*

	T (K)	α_{11}	α_{22}	α_{33}	α_{23}	α_{13}	α_{12}
I	283–320	74 (1)	30 (2)	28 (2)	–15 (1)	–49 (1)	26 (1)
II	283–320	74 (3)	30 (4)	29 (4)	–15 (3)	–50 (3)	26 (3)

of approximately 0.5 mm, using equipment similar to that used on the LHPM crystal.

Table 5 lists the Bragg angles recorded at two temperatures and Table 6 gives the components α_{ij} calculated using method I (upper row) and method II (lower row). For this example, the precision of the results using method II is also lower, by a factor of two, compared to those obtained using method I.

Discussion

An obvious advantage of method I is that it is not necessary to determine the absolute values of the lattice constants, the small changes of which yield the thermal expansion. Systematic errors in the absolute θ values will cancel if only the difference in θ is used, as in method I.

An essential difference between the two methods is the extent to which the propagation of the uncertainties of the measured Bragg angles, $\Delta\theta_m$, affects the final α_{ij} values. In method I, their errors, $\Delta\alpha_{ij}$, are derived directly from the least-squares procedure. In method II, the least-squares procedure yields, first, the standard deviations of the lattice constants and these are further propagated to the errors of α_{ij} .

For the calculation of the propagation of errors, the standard formula assuming Pythagorean addition of the different fractional standard deviations of the various contributing quantities was adopted. This formula is valid only under the explicit assumption that the uncertainties of the different quantities are mutually independent and randomly distributed (see, for example, Taylor, 1982). If these conditions are not fulfilled, the propagated errors are larger. Under the assumptions mentioned, methods I and II should yield results of equal precision which was proven by simulating calculations using data sets with artificially and randomly generated errors.

Our experimental results show clearly the superiority of method I. This means that, in practice, the data are affected by non-random errors and that the contributing quantities are not independent. Such systematic errors can be caused, for example, by zero shift, eccentricity, absorption, refraction and crystal tilt (Bond, 1960). This was verified by model calculations with artificially introduced systematic errors. One point of practical importance should be added. Relatively large single-crystal specimens should be used in order to obtain an acceptable signal-to-noise ratio for reflections in the high- θ region; on the other

hand, sizeable specimens introduce some of the systematic errors mentioned above.

The program ALPHA

To perform the calculations to method I, a Fortran program was written which has been tested on a DEC PDP10, a MicroVAX and an IBM PC. It can be applied for all crystal systems (except the cubic system as a trivial case). The input file consists of the Bragg angles measured at different temperatures. The output lists the tensor components, their eigenvalues and eigenvectors (*i.e.* the directions of the principal axes) and the coordinates of the latter in a stereographic projection. If desired, the principal values α_{ii} , as functions of temperature, can be fitted by polynomials up to the third order. All calculations are accompanied by an appropriate error analysis. A copy of this program can be obtained on request from the authors. A similar program has been written by Calvarin & Weigel (1972), but this is restricted to monoclinic crystals.

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