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Thermal Expansion of Manganese Carbonate

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Precision lattice parameters of manganese carbonate have been determined at different temperatures by the X-ray powder method in the temperature range 28 to 265° C. The data has been used to evaluate, by a graphical method, the two coefficients of thermal expansion, $\alpha_{\parallel}$ along the *c*-axis and $\alpha_{\perp}$ at right-angles to the *c*-axis. The temperature-dependence of the coefficients is represented by the following equations:

$$\alpha_{\parallel} = 22.942 \times 10^{-6} - 5.555 \times 10^{-8}T + 3.361 \times 10^{-10}T^2, \quad (1)$$

$$\alpha_{\perp} = 0.740 \times 10^{-6} + 2.812 \times 10^{-8}T - 6.722 \times 10^{-12}T^2, \quad (2)$$

where T is the temperature in ° C.

As a part of a programme of X-ray studies on calcite type compounds, the authors have determined the precision lattice parameters and the coefficients of thermal expansion of manganese carbonate at various temperatures. The results obtained on some crystals of this type namely, calcite [1], magnesium carbonate [2] and sodium nitrate [3] have already been published. When the work was under progress, Moreau [4] using copper radiation studied the variation in the lattice parameters of synthetically prepared manganese carbonate and evaluated the average coefficients of thermal expansion in the temperature range 20 to 270° C. He made use of reflections with Bragg angles of less than 45°. No reports could be found in the literature on the thermal expansion of naturally occurring manganese carbonate.

Transparent natural single crystals of manganese carbonate of rhombohedral shape, were kindly supplied to us by Dr R. Stevenson, Director, Magnetic Laboratory, Quebec, Canada. Single crystals were made into powder and the specimen was prepared by pasting the powder to a thin pyrex rod using Quickfix. The powder pattern showed no extra lines due to impurities. Using a 19 cm high-temperature camera, powder photographs were taken with FeK radiation from a Raymax-60 demountable X-ray unit, at different temperatures ranging from the room temperature to the dissociation temperature. The heavy fluorescent radiation observed on the diffraction photographs was eliminated by using thin aluminium foils. Seven reflections $(1.1.12)_{\alpha_1}$, $(3\,1\,4)_{\alpha_1}$, $(2\,2\,6)_{\alpha_1}$, $(4\,0\,4)_{\alpha_1}$, $(4\,0\,4)_{\alpha_2}$, $(3\,1\,8)_{\alpha_1}$ and $(3\,1\,8)_{\alpha_2}$ recorded in the Bragg angle region 57 to 78° were used in evaluating the lattice parameters at different temperatures. The experimental details and the method of evaluating the precision lattice parameters and the coefficients of thermal expansion have been described in an earlier paper [1].

Lattice parameters obtained at different temperatures are given in table I and shown graphically in fig. 1. The lattice parameters at room temperature obtained in the present investigation are compared with the earlier values in table II.

TABLE I Lattice parameters of $MnCO_3$ at various temperatures

Temperature, °C	*a*, Å	*c*, Å
30	4.7719 ± 0.0003	15.6443 ± 0.001
78	4.7724 ± 0.0003	15.6639 ± 0.001
132	4.7730 ± 0.0003	15.6774 ± 0.001
165	4.7745 ± 0.0003	15.6910 ± 0.001
215	4.7757 ± 0.0003	15.7087 ± 0.001
232	4.7762 ± 0.0003	15.7091 ± 0.001
265	4.7760 ± 0.0003	15.7316 ± 0.001

TABLE II Lattice parameters of $MnCO_3$ at room temperature

Author	a, Å	c, Å
Swanson *et al* [5]	4.777	15.67
Graf [6]	4.7771	15.664
Moreau [4]	4.7758	15.6676
Present study	4.7719 ± 0.0003	15.6443 ± 0.001

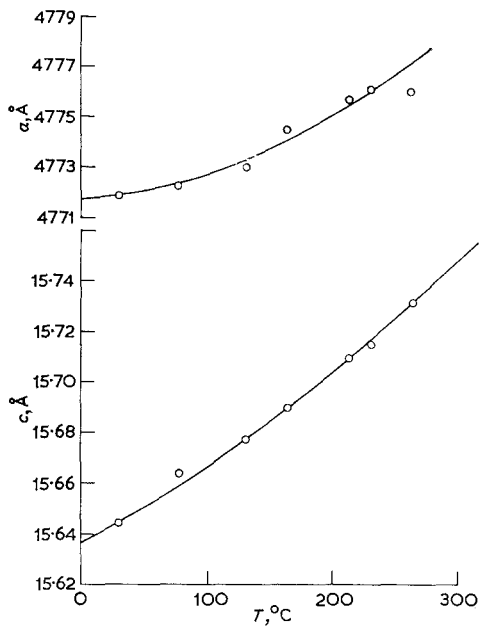

Figure 1 Variation of the lattice parameters of $MnCO_3$ with temperature.

The temperature-dependence of the coefficients of thermal expansion $\alpha_{\parallel}$ along the c-axis and $\alpha_{\perp}$ at right-angles to the c-axis are represented by the equations 1 and 2.

$$\alpha_{\parallel} = 22.942 \times 10^{-6} - 5.555 \times 10^{-8}T + 3.361 \times 10^{-10}T^2, \quad (1)$$

$$\alpha_{\perp} = 0.740 \times 10^{-6} + 2.812 \times 10^{-8}T - 6.722 \times 10^{-12}T^2, \quad (2)$$

where T is the temperature in ° C. The observed coefficients of expansion at different temperatures are given in table III along with the calculated values obtained from equations 1 and 2.

The lattice parameters at room temperature obtained in the present study are slightly lower than the values obtained by other investigators. The mean expansion coefficients of manganese carbonate between 30 and 265°C obtained from the present data are $\alpha_{\perp} = 3.61 \times 10^{-6}$ ° C^{-1} and $\alpha_{\parallel} = 23.63 \times 10^{-6}$ °C^{-1} and those obtained by Moreau [4] are $\alpha_{\perp} = 1.93 \times 10^{-6}$ ° C^{-1} and

TABLE III Coefficients of expansion of $MnCO_3$ at different temperatures

Temperature, °C	$\alpha_{\perp} \times 10^6$ Obs.	Calc.	$\alpha_{\parallel} \times 10^6$ Obs.	Calc.
40	1.78	1.85	19.17	21.26
60	2.51	2.40	20.13	20.82
80	3.03	2.95	20.45	20.65
100	3.35	3.49	21.09	20.75
120	3.98	4.02	21.73	21.12
140	4.61	4.55	23.65	21.75
160	5.02	5.07	23.97	22.66
180	5.65	5.58	25.24	23.83
200	6.07	6.09	25.89	25.28
220	6.60	6.60	27.16	26.99
240			28.12	28.97
260			28.76	31.22

$\alpha_{\parallel} = 59.33 \times 10^{-6}$ °C^{-1}. Even though there is agreement in the value of $\alpha_{\perp}$ there is a large difference in the value of $\alpha_{\parallel}$. This may be due to errors in the observations of Moreau [4], as he has used reflections with a Bragg angle of about 45° only. As Fe radiation has been used in the present investigation, reflections in the high Bragg angle region could be recorded.

The thermal behaviour of manganese carbonate is similar to the other compounds of calcite type in having a relatively large coefficient of expansion along the c-axis which is normal to the CO_3 layers and a small coefficient of expansion in the perpendicular direction.

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