TABLE II The values of $\langle D_{\text{eff}} \rangle$ for 111 and 311 reflections, when the solution treatment temperature is 450° C.

Ageing time (min)	Effective size of Ge precipitates (Å)				R.m.s. microstrains for 111 reflection at $3\delta = 55$ Å, and 311 reflection at $3\delta = 68$ Å ($\times 10^{-3}$)	
	$\langle \epsilon_n^2 \rangle = 0$		$\langle \epsilon_n^2 \rangle = C/n$			
	$\langle D_{\text{eff}} \rangle_{111}$	$\langle D_{\text{eff}} \rangle_{311}$	$\langle D_{\text{eff}} \rangle_{111}$	$\langle D_{\text{eff}} \rangle_{311}$	$\langle \epsilon_3^2 \rangle_{111}^{1/2}$	$\langle \epsilon_3^2 \rangle_{311}^{1/2}$
390	61	78	101	135	9·3	2·8
1200	66	86	121	147	8·5	2·9
3000	69	87	124	150	7·7	2·7

depends on the error arising mainly from inaccurate estimation of the background intensity. Because the total amount of Ge precipitates is relatively low in a specimen, the counting rates in the measurements are not very high. The counting rate of the 311 reflection is lower than that of the 111 reflection, thus the values of $\langle D_{\text{eff}} \rangle_{111}$ are more accurate than those of $\langle D_{\text{eff}} \rangle_{311}$. Fourier analysis of X-ray diffraction line profiles is a useful method for the study of precipitation in alloys provided that the microstrain and the particle size components in the Fourier coefficients can be separated.

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Anomalous expansion of cadmium carbonate

Cadmium carbonate crystallizes in the space group $R\bar{3}C$ and is isotypic with the calcite group, a family of AXO_3 compounds in which the XO_3 ions are planar. Though many investigators, Ramdohr and Strunz [1], Swanson *et al.* [2] and Graf [3] report the lattice parameters of cadmium carbonate at room temperature, the accuracy of the values is not high. When this work was under progress, Bayer [4] using copper radiation studied the variation in the lattice parameters of cadmium carbonate and evaluated the average coefficients of thermal expansion in the temperature range 20 to 320° C. He made use of reflections with Bragg angles in the range 20 to 40° and reported negative coefficient of expansion along the *a*-direction. No other reports could be found in the literature on the thermal expansion of cadmium carbonate.

The sample used in the present study was supplied by E. Merck, Germany. The powder sample for the study was prepared by filling it in a thin-walled quartz capillary. Using a Unicam 19 cm high-temperature camera, powder photographs were taken with Fe*K* radiation from a Raymax-60 X-ray unit. It was found that due to the fine particle size of the sample, high angle reflections were not sharp. Repeated annealing of the sample at 250° C improved the pattern slightly. With Cu radiation, a considerable overlap of the reflections is observed in the high Bragg angle region. Hence, Fe*K* radiation is preferred. Details of the experimental technique and the method of evaluating the precise lattice parameters and the coefficients of thermal expansion have been described in an

TABLE I Lattice parameters of $CdCO_3$ at different temperatures

Temperature (°C)	a (Å)	c (Å)
30	4.9226	16.2914
65	4.9219	16.3015
96	4.9212	16.3113
165	4.9220	16.3421
217	4.9230	16.3577
237	4.9235	16.3611
267	4.9243	16.3885
297	4.9254	16.4013

earlier paper [5]. Five reflections $(3.1.10)_{\alpha_1}$, $(3\,1\,4)_{\alpha_1}$, $(2\,2\,6)_{\alpha_1}$, $(4\,0\,4)_{\alpha_1}$ and $(3\,1\,8)_{\alpha_1}$ recorded in the Bragg angle region 57° and 71° were used for evaluating the lattice parameters at different temperatures.

The lattice parameters at different temperatures are given in Table I. Initially, the a parameter decreased up to 96° C and then increased with increasing temperature. The mean standard deviation of the lattice parameter at different temperatures was found to be about 0.003 Å in the a parameter and about 0.001 Å in the c parameter. 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 Equations 1 and 2.

$$\alpha_{\parallel} = 18.241 \times 10^{-6} + 2.647 \times 10^{-8}\, T + 1.173 \times 10^{-10}\, T^2 \tag{1}$$

$$\alpha_{\perp} = -2.325 \times 10^{-6} + 4.725 \times 10^{-9}\, T + 1.202 \times 10^{-10}\, T^2 \tag{2}$$

where T is the temperature in °C.

The values of $\alpha_{\parallel}$ and $\alpha_{\perp}$ obtained at different temperatures are given in Table II along with values calculated from Equations 1 and 2.

It can be seen from the Table II that $\alpha_{\perp}$ is negative at room temperature and numerically decreases up to 90° C. At 90° C it changes sign, becomes positive and then increases up to 250° C.

TABLE II Coefficients of expansion of $CdCO_3$ at different temperatures

Temperature (°C)	$\alpha_{\parallel} \times 10^6$		$\alpha_{\perp} \times 10^6$	
	Obs.	Calc.	Obs.	Calc.
50	20.10	19.86	−3.05	−1.79
90	21.03	21.57	−0.86	−0.93
130	23.96	23.66	1.26	0.32
210	29.15	28.97	4.06	3.96
250	32.07	32.19	5.84	6.36

TABLE III Lattice parameters of $CdCO_3$ at room temperature

Reference	a (Å)	c (Å)
Ramdohr and Strunz [1]	4.92	16.27
Swanson *et al.* [2]	4.93	16.270
Graf [3]	4.9204	16.298
Present study	4.9226	16.2914

In Table III, the room temperature lattice parameters obtained in the present study are compared with those available in the literature. There is agreement between the values of the present study and those reported by Graf [3].

The mean expansion coefficients of cadmium carbonate obtained in the present study are:

$$\alpha_{\perp 30-96^\circ \mathrm{C}} = -4.37 \times 10^{-6}\, (^\circ\mathrm{C})^{-1},$$

$$\alpha_{\perp 96-297^\circ \mathrm{C}} = 4.25 \times 10^{-6}\, (^\circ\mathrm{C})^{-1}$$

and

$$\alpha_{\parallel 30-297^\circ \mathrm{C}} = 25.26 \times 10^{-6}\, (^\circ\mathrm{C})^{-1}$$

and obtained by Bayer [4] in the temperature range 20 to 320° C are:

$$\alpha_{\perp} = -5.6 \times 10^{-6}\, (^\circ\mathrm{C})^{-1}$$

and

$$\alpha_{\parallel} = 22.7 \times 10^{-6}\, (^\circ\mathrm{C})^{-1}.$$

Even though there is an agreement in the value of $\alpha_{\parallel}$ there is a large difference in the value of $\alpha_{\perp}$. This may be due to the errors in the observation of Bayer [4] as he has used reflections with Bragg angles between 20 and 40°. As Fe radiation has been used in the present investigation, reflections in the high angle region could be recorded.

In calcite type compounds, the cation radius of 0.99 appears to be critical. Below the cation radius of 0.99, a number of carbonates, borates and nitrates crystallize in the calcite structure.

The values of $\alpha_{\perp}$ [5–8] and cation radius are shown in Fig. 1. It can be seen that, in general, the coefficient of thermal expansion ($\alpha_{\perp}$) decrease with increasing cation radius. The values of $\alpha_{\perp}$ for nitrates are large and they decrease with increasing cation radius. It may be mentioned that the value of $\alpha_{\perp}$ is negative when the cation radius is very

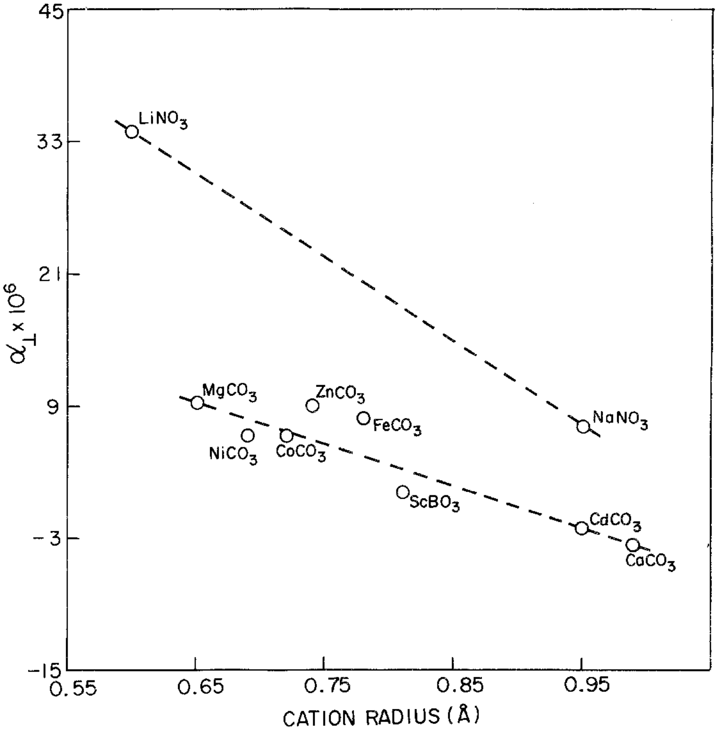

Figure 1 $\alpha_\perp$ versus cation radius.

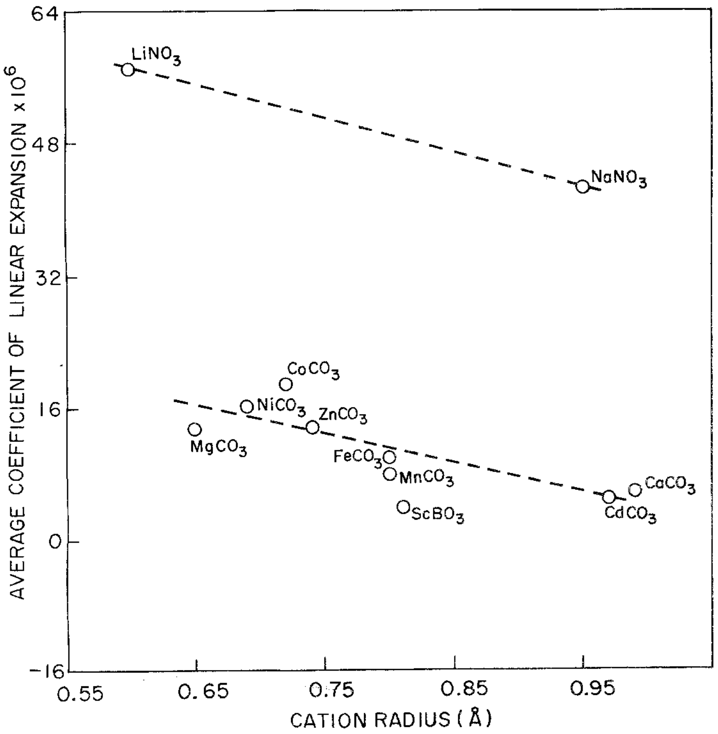

Figure 2 Average coefficient of linear expansion versus cation radius.

large. The average coefficient of linear expansion of calcite type compounds versus cation radius is shown in Fig. 2. It can be seen from the graph that the average coefficient of linear expansion decreases linearly with increasing cation radius. This plot also shows that the average coefficients of linear expansion of nitrates are high and decrease with increasing cation radius.

Kaga [9] observed a similar linear relationship between the third order elastic constants and the lattice parameter 'a'. It may be mentioned that there is a linear increase of a, c and the volume of the unit cell of the calcite type compounds with increase in cation radius.

Angino [10], from his far infrared spectra data on calcite type compounds, concluded that there exists a linear relationship between the frequency of certain lattice mode vibrations and the cation radius. Similar observations were also reported by Haung and Kerr [11], Weir and Lippincott [12] and Adler and Kerr [13].

The negative expansion value of $\alpha_\perp$ at room temperature in the case of cadmium carbonate which has 0.97 cation radius is in agreement with the above linear relationship.

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