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Thermal Expansion of Synthetic Aragonite Condensed Review of Elastic Properties

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Samples of pure aragonite are synthesized by precipitation from aqueous solution and used to determine the heat capacity and temperature dependence of the unit cell parameters in the temperature range 291–700 K. The X-ray diffraction powder diagram at room temperature is refined in space group *Pnma* and resulted in the cell parameters $a = 5.7444(8)$ Å, $b = 4.9620(4)$ Å, $c = 7.9700(6)$ Å, and $V = 227.17(3)$ Å^3. TRXD allows the study of the thermal expansion of the lattice up to the phase transition to the stable calcite which occurs at 723 K. Anisotropic expansion coefficients are computed in the temperature ranges 291–700 K and 800–900 K for aragonite and calcite, respectively. From heat capacity measurements and high pressure compressibility data from the literature, some elastic coefficients of aragonite and calcite, particularly those of the Grüneisen type, are reexamined. © 1999 Academic Press

Key Words: **calcium carbonate; synthetic aragonite; transition to calcite; thermal expansion; Grüneisen coefficients.**

INTRODUCTION

Five polymorphic modifications of crystalline anhydrous calcium carbonate are described in the literature; calcite I (simply called calcite), calcite II, calcite III, vaterite, and aragonite which are stable in specific temperature and pressure ranges. The Clapeyron diagram $P(T)$ is well known for the solid state equilibrium calcite ⇔ aragonite. The equilibrium pressure for the reversible transformation is within the interval 240–410 MPa at room temperature. At and above this pressure aragonite is in its steady state. Under room pressure conditions, only calcite is thermodynamically stable (1–4).

The formation of metastable vaterite and aragonite under ambient pressure results from interferences of kinetic factors in the equilibrium process (5, 6). Aragonite crystallization occurs frequently in nature (shells, corals, mineral sediments, etc.). It is usually stabilized by the presence of ionic species such as Mg^{2+} (7) or Sr^{2+} (8) in the crystallization medium. The preparation of the pure aragonite phase at ambient pressure in the absence of additives is difficult but can be achieved under well-controlled conditions.

This paper deals with an improved characterization of a pure synthetic aragonite prepared originally with the aim of processing a new porous material for bone replacement (9).

EXPERIMENTAL

Material Preparation

Aragonite was prepared by precipitation from aqueous solutions of potassium hydrogenocarbonate and calcium chloride. The stirred 0.1 M solutions were brought to boiling before mixing. The carbonate precipitate was then quickly filtrated, washed, and dried at 110°C (9, 10). The purity of the product was checked by X-ray powder diffraction. When no peak of calcite or vaterite was detectable, the aragonite was considered as pure. The two other modifications of $CaCO_3$ (calcite and vaterite) were then present with a molar concentration of at most a few molar percent or absent. Samples of pure aragonite are in the form of a white powder with needle-like grains of an average length of 5 to 10 μm and an average width of 1 to 2 μm.

X-Ray Analysis

A powder X-ray analysis has been carried out at 291 ± 1 K with a Siemens D500 diffractometer in the Bragg–Brentano geometry. A monochromatic Cu$K\alpha_1$ radiation ($\lambda = 1.54059$ Å) was produced with an incident beam monochromator as a curved-crystal of germanium. The alignment of the diffractometer was checked by means of standard reference materials and the zero error was less than 0.01°(2θ). The diffraction pattern was scanned over the

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angular range 19–80°(2θ) with a step size of 0.02°(2θ) and a count time of 16 s per step.

The crystallographical characterization of the aragonite to calcite transition under ambient pressure was performed by temperature resolved X-ray diffractometry (TRXD) by means of an INEL (CPS 120) cylindrical position sensitive detector used in a semifocusing geometry by reflexion (monochromatic Cu$K\alpha_1$ radiation) (11). The sample was stationary and located at the center of the goniometer in a monitored high temperature furnace. The powder was deposited as a thin layer on a nickel grid in order to avoid mass effects during heating. The PSD mode of the data acquisition reached a spatial resolution of about 0.03°(2θ) for a count time of 1200 s.

In order to ascertain TRXD data, additional X-ray measurements at high temperatures were performed using a conventional two-axis goniometer. The device is made of a SIEMENS diffractometer with a diffracted-beam monochromator (Cu$K\alpha_{1,2}$) equipped with a furnace.

Thermal Analysis

The heat content $C_p(T)$ under ambient pressure was measured in a differential scanning calorimeter Perkin–Elmer DSC7 using a sapphire reference. Samples 70–80 mg in weight were heated from 40 to 300°C at a rate of 300°C per hour in a calibrated aluminum crucible. The heat content per gram was directly measured and computed (12).

RESULTS AND DISCUSSION

Room Temperature X-Ray Powder Diffraction Pattern

The angular peak positions $2\theta_{\text{obs}}$ and interspacings d_{obs} were calculated by a fitting program and are fully evaluated. The first 27 observed lines are indexed in space group *Pnma* (no. 62) with the successive dichotomy method using the code DICVOL GV91 (13). The peak of weak intensity $I/I_0 = 0.05$ observed at $2\theta_{\text{obs}} = 45.475°$ which is not mentioned in the JCPDS file of aragonite no. 41.1475 is indexed as line 004 in this latter space group (14).

A least-squares refinement of the orthorhombic unit cell parameters was performed by means of the code NBS*AIDS 90 (15) and resulted in the following parameters $a = 5.7444(8)$ Å, $b = 4.9620(4)$ Å, $c = 7.9700(6)$ Å, and $V = 227.17(3)$ Å^3 [$M_{20} = 48.9$; $F_{29} = 50.0$ (0.0094; 62)]. The resulting crystallographic density for $Z = 4$ is 2.926. A powder dried 72 h at 110°C has an experimental density 2.919 ± 0.009 at 27°C measured with an He Pycnometer, ACCUPYC 1330.

Considering these new data, a Rietveld refinement of the structure was performed. The stability was obtained with $R_{\text{wp}} = 0.16$ and $R_{\text{f}} = 0.04$, taking into account a strongly preferred orientation of the needle-like grains along their a-axis. Atomic coordinates and associated geometric parameters were in agreement with previous results (16, 17).

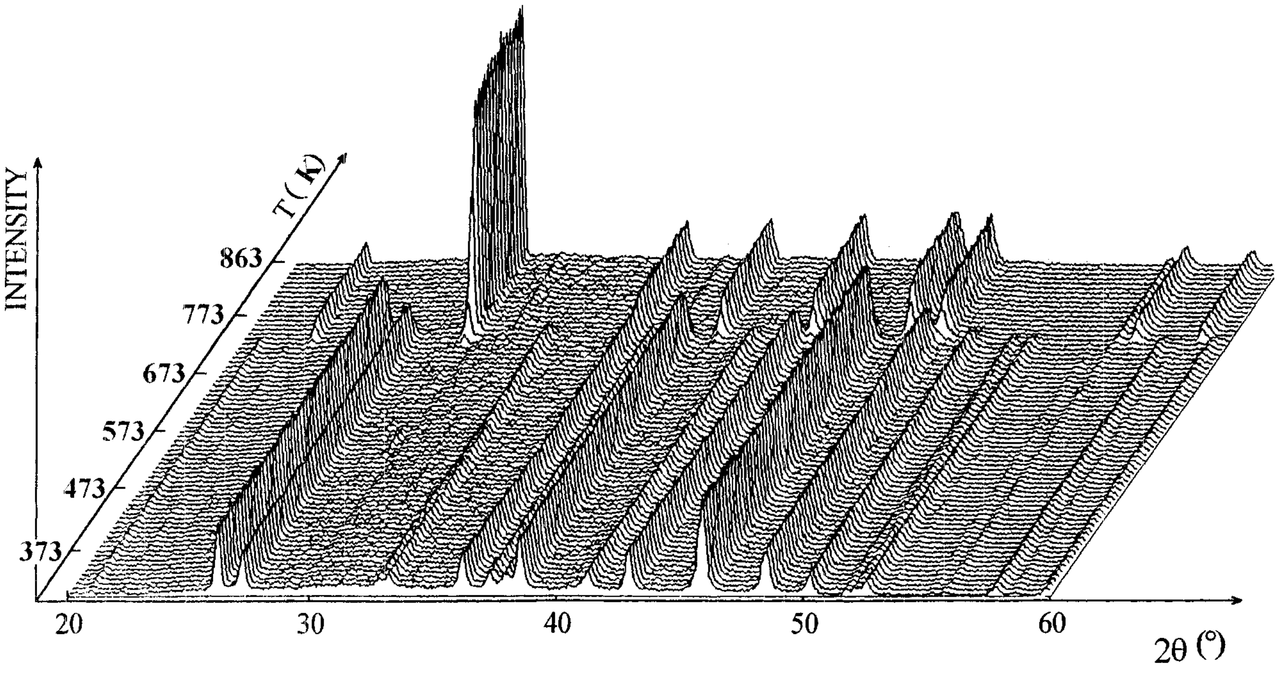

FIG. 1. TRXD of the transition from metastable aragonite to stable calcite modification of calcium carbonate for a heating rate of 25° per hour.

TABLE 1
Refined Cell Parameters at Different Temperatures

T (K)	a (Å)	b (Å)	c (Å)	V (Å^3)
Aragonite				
291^a	5.7491(8)	4.9619(6)	7.9696(8)	227.35(3)
382^a	5.7631(16)	4.9669(9)	7.9809(15)	228.45(6)
452^a	5.7764(10)	4.9706(9)	7.9923(11)	229.47(5)
534^a	5.7902(14)	4.9730(11)	8.0045(14)	230.49(6)
611^a	5.8112(18)	4.9766(10)	8.0156(18)	231.81(7)
692^a	5.8326(22)	4.9798(14)	8.0315(20)	233.28(9)
291^b	5.7444(8)	4.9620(4)	7.9700(6)	227.13(3)
473^b	5.7794(9)	4.9713(8)	7.9984(10)	229.80(4)
673^b	5.8285(6)	4.9822(5)	8.0327(8)	233.25(3)
Calcite				
769^a	4.980(2)		17.30(1)	371.6(3)
809^a	4.980(2)		17.32(1)	372.2(3)
848^a	4.982(2)		17.354(9)	373.0(2)
863^a	4.983(2)		17.36(1)	373.4(3)

[a] Experimental data from TRXD.
[b] Experimental data from conventional diffractometry.

Aragonite to Calcite Phase Transition

A 3D representation of the successive powder diffraction patterns with increasing temperature is shown in Fig. 1. The spontaneous transition is observed at 450°C (723 K) for a heating rate of 25°C per hour.

The transition temperature of aragonite to stable calcite at ambient air pressure is known to be influenced by procedural variables, by composition and origin of the product. In the present case, the transition temperature is higher than in the case of water containing aragonite from coral or aragonite mixed with 5% of calcite. It is close to the transition temperature of well-crystallized aragonite of mineral origin and of pure synthetic aragonite obtained with a different preparation technique (18, 19).

Anisotropic Expansion Coefficients

Cell parameters were refined by means of the same codes DICVOL GV91 and NBS*AIDS 90 as in the section above, from data collected by TRXD and conventional diffractometry (Table 1). Their evolution versus temperature is presented in Figs. 2 and 3 for aragonite and calcite, respectively. For aragonite, a parabolic plot is chosen for $a(T)$ and $V(T)$. A simply linear correlation seems to be suited for $b(T)$ and $c(T)$. Only linear variations are considered for calcite cell parameters.

Anisotropic expansion coefficients have been determined from these parabolic and linear fits. The values of $\alpha_a = 1/a.(\partial a/\partial T)_P$ and $\alpha_V = 1/V.(\partial V/\partial T)_P$ over the temperature

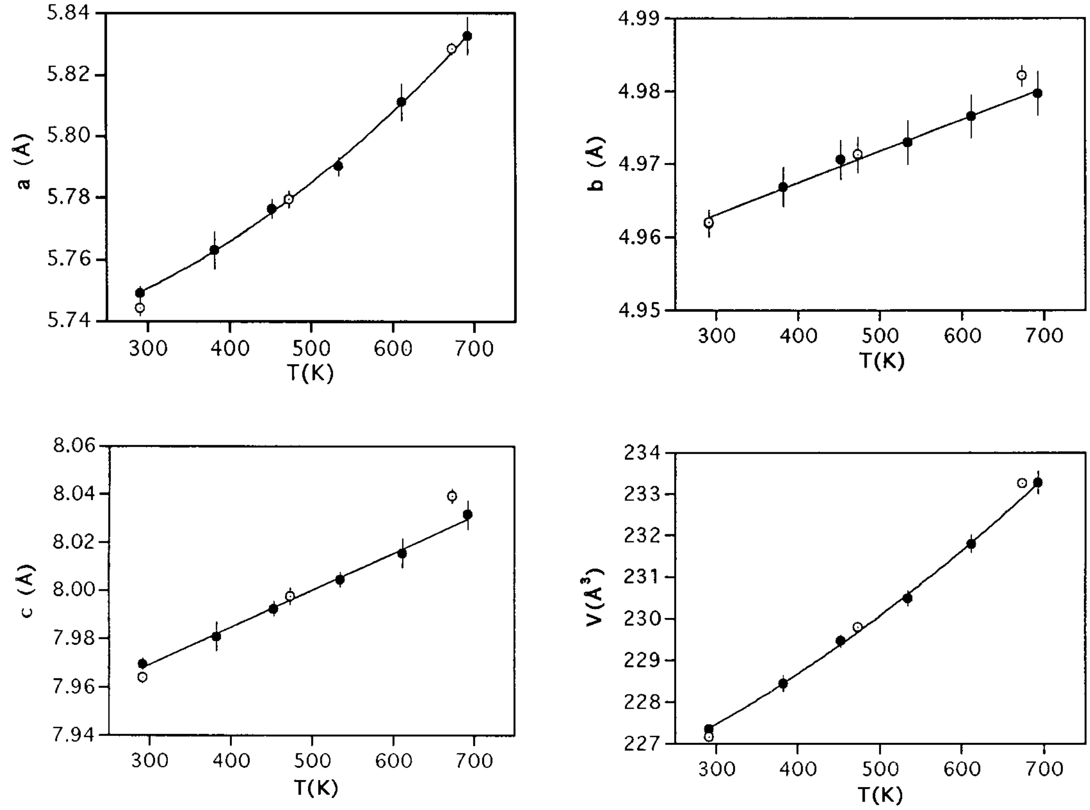

FIG. 2. Parabolic and linear plot of cell data of aragonite as functions of the temperature in the range 291–692 K under $P = 1$ atm; (●) experimental data from TRXD; (○) calibration data from conventional diffractometry.

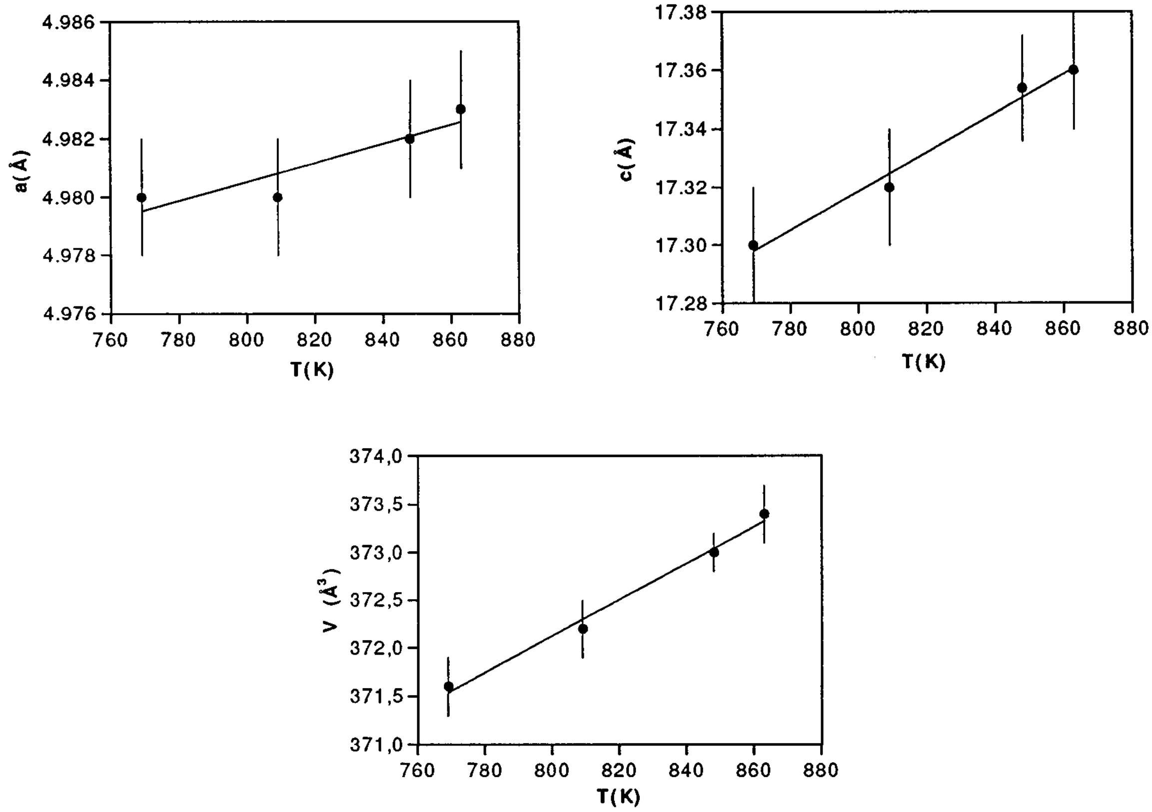

FIG. 3. Linear plot of cell parameter data of calcite as functions of the temperature in the range 769–869 K under $P = 1$ atm.

range 291–700 K for orthorhombic aragonite are presented in Table 2. Over this range, the mean values of $\alpha_b = 1/b \cdot (\partial b/\partial T)_P$ and $\alpha_c = 1/c \cdot (\partial c/\partial T)_P$ are $(8.8 \pm 1.1) \times 10^{-6}\,\mathrm{K}^{-1}$ and $(19.2 \pm 1.7) \times 10^{-6}\,\mathrm{K}^{-1}$, respectively. The confidence limits are calculated presently with four degrees of freedom at the usual probability level 0.05.

A similar evaluation for calcite with only four data leads to the indicative values $\alpha_a = 6.5 \times 10^{-6}\,\mathrm{K}^{-1}$, $\alpha_c = 38.5 \times 10^{-6}\,\mathrm{K}^{-1}$, and $\alpha_V = 51 \times 10^{-6}\,\mathrm{K}^{-1}$.

TABLE 2
Anisotropic Expansion Coefficients of Aragonite under Ambient Pressure: Smoothed Values with Their Confidence Limit

T (K)	10^6 ($\alpha_a \pm 0.3$) (K^{-1})	10^6 ($\alpha_v \pm 1.0$) (K^{-1})	T (K)	10^6 ($\alpha_a \pm 0.4$) (K^{-1})	10^6 ($\alpha_v \pm 1.0$) (K^{-1})
291	22.1	48.1	600	43.1	72.0
300	22.8	48.8	650	46.4	75.7
400	29.6	56.7	700	49.7	79.4
500	36.4	64.4			

Reexamination of Some Elastic Coefficients of Aragonite and Calcite

A condensed review of compressibility, expansion, and heat content is listed in Table 3. There is a lack of information on thermodynamic properties of synthetic aragonite at room temperature (20). In the compilation (21), heat capacity is strictly identical for calcite and aragonite, namely C_p (298 K) = 81.87 $\mathrm{JK}^{-1}\,\mathrm{mol}^{-1}$ and C_p (723 K) = 115.50 $\mathrm{JK}^{-1}\,\mathrm{mol}^{-1}$.

A reexamination of heat content was performed between 323 and 578 K on freshly prepared powdered aragonite by a set of calorimetric measurements. This study is quite similar to those performed for a high-T_c superconductor cited in Ref. (22). A typical recording $C_p(T)$ is depicted in Fig. 4, where it can be compared with the smoothed variation previously reported by Knacke *et al.* (21).

The least squares correlation $C_p = 121.25–14.04 \times 10^{-3}\,\mathrm{T}–32.45 \times 10^5\,\mathrm{T}^{-2}$ ($\mathrm{JK}^{-1}\,\mathrm{mol}^{-1}$) was computed with 29 data points (C_p, T). It allows the calculation of C_p within a confidence limit $\pm 0.5\,\mathrm{JK}^{-1}\,\mathrm{mol}^{-1}$ at the probability threshold 0.05. The values $C_p(298\,K) = 80.52\,\mathrm{JK}^{-1}\,\mathrm{mol}^{-1}$ and $\mathrm{C}_p(723\,\mathrm{K}) = 104.89\,\mathrm{JK}^{-1}\,\mathrm{mol}^{-1}$ can then be calculated

TABLE 3
Condensed Review of Elastic Coefficients of Aragonite and Calcite at 298 and 723 K

Aragonite			Calcite		
High pressure compressibility χ_v $(T) = -1/V\,(\partial V/\partial P)_T$ $(10^{-12}\,Pa^{-1})$(1, 2, 25–29)					
χ_v (298) = 15.2(2, 26) 15.5(31)			χ_v(298) = 12.8(2, 26); 22.1(27); 16.8(29); 13.7(28)		
χ_v (723) = 20.0 evaluated (1, 26, 30)			χ_v(723) = 25.0(27); 15.8 extrapolated(28); 15.8(29)		
Volumic expansion coefficient α_v (T) = $1/V\cdot(\partial V/\partial T)_P$ $(10^{-6}\,K^{-1})$(2, 25, 27, 29)					
α_v (298) = 48.1^c; 64.0(2)			α_v (298) = 20.0(2); 13.1(27); 25.2(29)		
α_v (723) = 81.4^c; 64.5 extrapolated (2)			α_v (723) = 22.0(2); 28.9(27); 38.2(29)		
Molar volume V(T) $(10^-6\,m^3$(mole of mean atom)$^{-1}$)					
V (298) = 6.8487^c			V (298) = 7.3827(32); 7.3532(2)		
V (723) = 7.0350^c			V (723) = 7.4453(32) evaluated; 7.4180(2)		
Molar heat content C_v (JK^{-1}(mole of mean atom)$^{-1}$ (^{c}, 20, 21, 23, 24, 33)					
	m^a	M^b		m^a	M^b
$[C_p - C_v]$(298)	0.31	0.56	$[C_p - C_v][$(298)	0.05	0.11
C_v (298)	15.5	15.8	C_v (298)	16.3	16.7
$[C_p - C_v]$ (723)	1.3	1.7	$[C_p - C_v]$ (723)	0.10	0.29
C_v (723)	19.3	19.9	C_v (723)	22.8	23.6
Mean Grüneisen coefficient $\gamma_0\,(T) = \alpha_v V/C_v\chi_v$(2, 3, 39, 33-35)					
	m^a	M^b		m^a	M^b
γ_0(298)	1.35	1.86	γ_0(298)	0.40	0.89
γ_0(723)	1.14	1.48	γ_0(723)	0.28	0.60

[a] Minimum value.
[b] Maximum value.
[c] Present work.

and are systematically lower than the precedent ones (20–24).

The negative sign of the T coefficient in this equation is remarkable. It results in a maximum of the representative curve for $T = 773$ K (500°C), not far from the transition temperature observed by TRXD. The present sample of synthetic aragonite powder exhibits a different behavior from natural aragonite from which most of the C_p data reported in the literature have been gathered. A so-called *anticipation* of the transition to calcite may be envisaged in the present case (4).

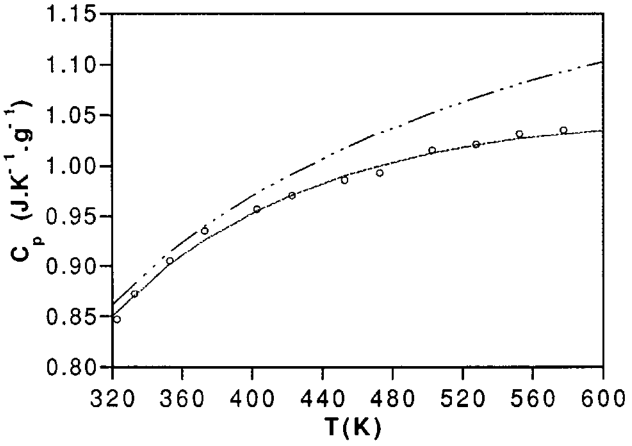

FIG. 4. Molar heat content of aragonite; (–·–·–) compiled data from tables[23], (–○–) adjusted fit of present experimental data.

In addition to the present new data, values of some elastic coefficients, particularly those of the isotropic Grüneisen type, are envisaged and tabulated in the framework of several studies of the thermal evolution of aragonite and calcite (22, 36, 37).

CONCLUSION

Because of the scattering of the coefficients in Table 3, the minimum and maximum values m and M of $(C_p - C_v) = T\alpha_v^2 V/\chi_v$, C_v, and the isotropic Grüneisen coefficient γ_0 are envisaged both for aragonite and calcite at room temperature and 723 K or 450°C, which is the spontaneous transition temperature of aragonite to calcite presently observed by TRXD.

Few experimental data of $\gamma_0(T)$ are available in the literature for aragonite. Salje and Wisnamathan (2) determined $\gamma_0(298\text{ K}) = 1.81$ and $\gamma_0(723\text{ K}) = 1.37$ as an extrapolated value. In the same paper, $\gamma_0(298\text{ K}) = 0.54$ and $\gamma_0(723\text{ K}) = 0.46$, also extrapolated, are proposed for calcite. Anisotropic coefficients γ_0 have been extensively studied for natural and synthetic calcite, principally by spectroscopy and theoretical calculations. Recently, Catti *et al.* (20) computed isotropic values $\gamma_0(300\,\mathrm{K}) = 0.624$ and $\gamma_0(500\ \mathrm{K}) = 0.509$.

It is obvious from the present work that accurate compressibility data concerning synthetic aragonite are required to characterize precisely the elastic phenomena at the phase transition from aragonite to calcite.

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