

LETTERS

Elasticity of single-crystal calcite and rhodochrosite by Brillouin spectroscopy

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ABSTRACT

The single-crystal elastic moduli of natural samples of both calcite (CaCO<sub>3</sub>) and rhodochrosite (MnCO<sub>3</sub>) have been measured by Brillouin spectroscopy under ambient condition. Based on the trigonal unit cell, the elastic constants  $C_{11}$ ,  $C_{33}$ ,  $C_{44}$ ,  $C_{12}$ ,  $C_{13}$ , and  $C_{14}$  are 149.4(7), 85.2(18), 34.1(5), 57.9(11), 53.5(9), -20.0(2), and 223.9(15), 132.6(41), 44.5(9), 93.4(21), 76.0(23), -17.3(6) GPa for CaCO<sub>3</sub> and MnCO<sub>3</sub>, respectively. Our data for calcite are in good agreement with earlier data obtained by ultrasonic experiments. The off-diagonal elastic constants ( $C_{12}$ ,  $C_{13}$ , and  $C_{14}$ ) for rhodochrosite have systematically larger values than the trend defined by other isostructural carbonates, in all of which the divalent cations are alkaline-earth metals. This is a distinctive signature of transition-metal-bearing oxides, which is present in silicates and simple oxides as well.

INTRODUCTION

A complete set of elastic constants for materials is important to estimate physical parameters such as the Debye temperature, compressibility and acoustic anisotropy. It is also well known that elastic properties of materials depend on pressure, temperature, chemical composition and crystal orientation. An important chemical variable is the presence of transition metal ions in oxides and silicates (Sumino 1979; Weidner et al. 1982; Zhang 1998; Zhang and Reeder 1999).

There are more than ten compounds which crystallize with the calcite-type structure at ambient conditions (e.g., Wyckoff 1964). Except for calcite (CaCO<sub>3</sub>), magnesite (MgCO<sub>3</sub>) and NaNO<sub>3</sub>, the elastic properties of the other calcite-type compounds are not available. Single-crystal elastic properties of calcite have been extensively studied, but exclusively by ultrasonic techniques (e.g., Dandekar 1968a, 1968b; Hearmon 1979; Vo Thanh and Lacam 1984). In the present study, we report the elastic properties of both calcite and rhodochrosite (MnCO<sub>3</sub>) as determined from Brillouin scattering measurements. The data for calcite thus obtained can be compared with those obtained by ultrasonic measurements, whereas the data for rhodochrosite are new results.

EXPERIMENTAL METHODS

The single crystals of both calcite and rhodochrosite used in the present work are natural samples. The calcite sample is Iceland spar and the pink rhodochrosite is from an unspecified locality in Mexico. The chemical composition of the latter was confirmed by electron probe analysis [(Mn<sub>0.98</sub>Mg<sub>0.01</sub>Ca<sub>0.01</sub>)CO<sub>3</sub>]. Both samples can be readily oriented using crystal morphology.

Calcite-type carbonates have perfect {100} cleavage in the trigonal cell (Fig. 1). A plate of calcite with parallel cleavage faces and a thickness of ~1 mm was carefully chosen for this study. The plate was optically clear and free from twins. The opposite faces of the calcite plate were not polished, and are parallel to each other within ±1°. There were many small cleavage cracks and twins inside the sample of rhodochrosite. Thus, a small optically clear plate (500 μm × 600 μm) with a thickness of ~200 μm was chosen for experiments. The opposite faces of the rhodochrosite plate were {100} cleavage faces and were finely polished to be parallel to each other within ±10'.

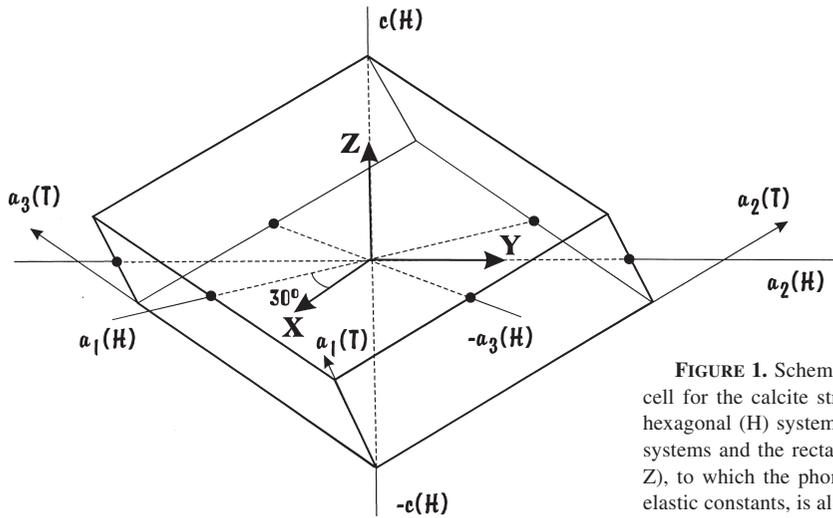
Samples thus prepared were then mounted on a three-circle Eulerian cradle, which was used to control the sample orientation. An argon ion laser (λ = 514.5 nm) and a six-pass tandem Fabry-Pérot interferometer were used for the Brillouin experiments. All measurements of acoustic velocities employed a symmetric scattering geometry with an external angle between the incident and scattered beams of 90°. With this geometry the refractive index can be cancelled out in the calculation of acoustic velocity, and the Brillouin frequency shift Δω is directly related to the acoustic velocity *V* and incident laser wavelength λ by

$$V = \Delta\omega\lambda / \sqrt{2} \quad (1)$$

In Brillouin scattering, the spectrum consists of an elastically scattered component with the same frequency as the excitation source and a set of inelastically scattered components. The latter display a frequency shift Δω caused by the interaction between photons and phonons in the sample. Details of the Brillouin scattering technique have been elucidated earlier (e.g., Sinogeikin and Bass 2000).

Brillouin data were also collected with the two sides of the sample plates reversed to reduce possible errors introduced by non-parallelism of the plate. A representative spectrum for MnCO<sub>3</sub> collected at the χ angle (about an arbitrary setting mark

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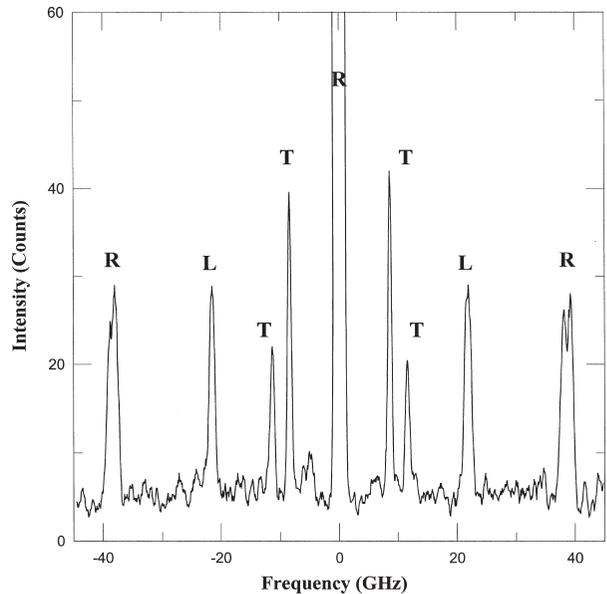
**FIGURE 1.** Schematic illustration of the cleavage rhomb pseudo-cell for the calcite structure described in both the trigonal (T) and hexagonal (H) systems. The relation between these crystallographic systems and the rectangular Cartesian coordinate system (X, Y, and Z), to which the phonon directions are referred in the inversion of elastic constants, is also shown.

on the three-circle Eulerian cradle) of  $345^\circ$  is displayed in Figure 2. As shown in this figure the Brillouin peaks were generally sharp and well defined. However, due to the strong birefringence of the two minerals studied, broad Brillouin peaks might be expected instead. This is because the scattering geometry for the “extraordinary wave” can be treated as symmetric only if the platelet is cut along a plane that is parallel to the threefold symmetry axis or if the projection of the optic axis on the scattering plane is perpendicular to the platelet faces. Except for a couple of special sample orientations, our samples do not satisfy these conditions. As a result, scattering that involves an extraordinary ray will have an error in phonon direction and velocity. The difference in frequency shift between the combination of ordinary-ordinary and extraordinary-extraordinary rays was estimated to be 2% or less for the platelets and geometry used in our experiments. Brillouin peaks of comparable intensity but differing by 2% in their shift would likely be observed as two overlapping peaks. The overlap of peaks with Brillouin shifts differing by 2% or less would be observed as a somewhat broadened single peak. Because we observed relatively sharp and well defined peaks, it is likely that the intensity contrast between the ordinary and extraordinary rays is large and that the observed scattering is dominated by the ordinary rays.

The observed acoustic velocities, along with the calculated phonon directions of (0, 1, 0) relative to the Cartesian coordinate system (Fig. 1), are illustrated in Figure 3 for a series of co-planer orientations. The final data sets for  $\text{CaCO}_3$  and  $\text{MnCO}_3$  consisted of 42 and 37 mode velocity determinations. Each data point is the average of three or more measurements from both sides.

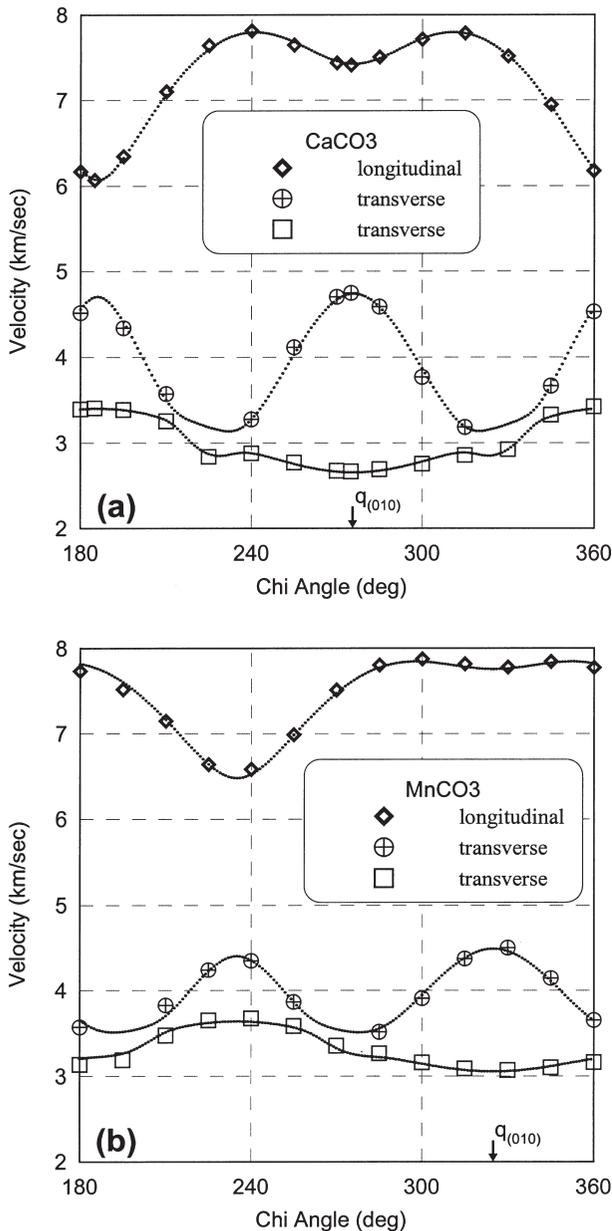
## RESULTS AND DISCUSSION

Throughout this study, all propagation direction of phonons lay approximately in the cleavage planes of both calcite and rhodochrosite. The normal vectors for the cleavage planes (which can be calculated from the cell parameters of samples)



**FIGURE 2.** Representative Brillouin spectrum of rhodochrosite, showing the frequency shift from the elastically scattered central Rayleigh peak, which is labeled R. Longitudinal and transverse acoustic modes are indicated by L and T, respectively.

relative to the chosen Cartesian system are thus (0.7024, 0, 0.7112) and (0.6874, 0, 0.7263) for  $\text{CaCO}_3$  and  $\text{MnCO}_3$ , respectively. Using these normal vectors and an initial set of estimated elastic constants, a least-squares algorithm was used to calculate the propagation directions of the observed phonons with an estimated accuracy of better than  $2^\circ$ . Because the sound velocity is a function of phonon direction and the density, we used a nonlinear inversion procedure to solve the Christoffel equations for the six elastic constants of trigonal  $\text{CaCO}_3$  and  $\text{MnCO}_3$ . The nonlinear inversion procedure uses the Gauss-



**FIGURE 3.** Longitudinal and transverse acoustic velocities as a function of  $\chi$  angle for (a) CaCO<sub>3</sub> and (b) MnCO<sub>3</sub>. All the measurements are in the cleavage plane {100}. Also labeled are the calculated phonon directions along (0, 1, 0) relative to the Cartesian system. Dotted lines are calculated from best-fit elastic moduli listed in Table 1. The root-mean-square deviations between calculated and measured velocities are 32 and 44 m/s for CaCO<sub>3</sub> and MnCO<sub>3</sub>, respectively.

Newton algorithm with Levenberg-Marquardt modifications for global convergence of solutions, and has been adopted widely in finding solutions to the Christoffel equations (e.g., Zha et al. 1996). Although the effect of uncertainties in the phonon directions could be amplified in solving the elastic tensor (Every 1980), after iterating the above two steps several times, the final values for both the phonon directions and elastic constants converged toward reliable results.

The elastic constants,  $C_{ij}$ , of calcite and rhodochrosite obtained in this work are listed in Table 1, together with other data for calcite-type carbonates for comparison. The results of our Brillouin experiment for calcite are in agreement with those of ultrasonic data. Because all of our acoustic velocity data were collected in a single crystallographic plane, this is a significant result. For non-cubic crystals, we normally collect data in at least two orthogonal planes. This approach maximizes the independence with which the elastic constants are determined, and minimizes co-variance between  $C_{ij}$  values. While these considerations remain valid, our results for calcite nevertheless give us a high degree of confidence in the reliability of elastic constants obtained from data collected in a single appropriately chosen crystallographic plane. This approach has previously been used with orthorhombic crystals by Duffy et al. (1995) and Zha et al. (1997).

Our data for rhodochrosite are consistent with the linear compressibility data on rhodochrosite recently reported by Zhang and Reeder (1999). These authors used X-ray diffraction of samples under pressure in a diamond anvil apparatus to study the axial compressibilities of rhodochrosite under high pressure. According to Nye (1957) and Franck and Wanner (1970), the change in length of a line at an angle  $\gamma$  to the trigonal axis under hydrostatic pressure (or the linear compressibility  $\beta$ ) is related to the elastic compliances  $s_{ij}$ , or the inverse of elastic stiffness tensor, as follows:

$$\beta = (s_{11} + s_{12} + s_{13}) - (s_{11} + s_{12} - s_{13} - s_{33}) \cos^2 \gamma \quad (2)$$

The logarithmic pressure derivative of the axis ratio  $c/a$  is thus related to the anisotropy of the linear compressibility by the following equation:

$$d \ln(c/a) / dP = s_{11} + s_{12} - s_{13} - s_{33} \quad (3)$$

Figure 4 displays the  $c/a$  ratio for MnCO<sub>3</sub> as a function of pressure as reported by Zhang and Reeder (1999). Our elastic moduli for MnCO<sub>3</sub> as listed in Table 1 yield a logarithmic pressure derivative for the  $c/a$  ratio of  $-3.56 \times 10^{-3} \text{ GPa}^{-1}$ , which is shown as a solid line in Figure 4 and is in good agreement with the  $c/a$  data.

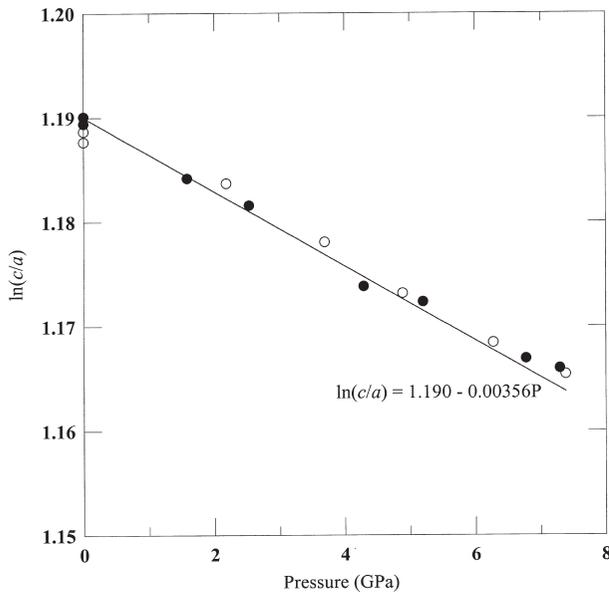
Our data for rhodochrosite enable us to evaluate the effect of 3d transition metal cations on elastic properties in carbonates proposed by Zhang and Reeder (1999). For the calcite-type carbonates, the elastic constants  $C_{ij}$  are available only for magnesite, rhodochrosite and calcite. Strictly speaking, dolomite [MgCa(CO<sub>3</sub>)<sub>2</sub>] is not a calcite-type structure. While the latter possesses space group  $R\bar{3}c$ , the former with space group  $R\bar{3}$  has a slightly lower symmetry. However, one may regard it as a special solid solution between magnesite and calcite in which the atoms along any threefold axis are alternatively Mg and Ca. The data for dolomite is also included in the present discussion, and this has consequently enabled us to make a qualitative evaluation of the role of Mg substitution for Ca in defining the elastic properties.

The values of  $C_{ij}$  for all these carbonates are plotted against the  $V$  in Figure 5. It is apparent that the three diagonal elastic constants  $C_{11}$ ,  $C_{33}$ , and  $C_{44}$  are approximately linearly and inversely related to the  $V$  for all these carbonates. Except for

**TABLE 1.** Elastic constants for four calcite-type carbonates (in GPa)

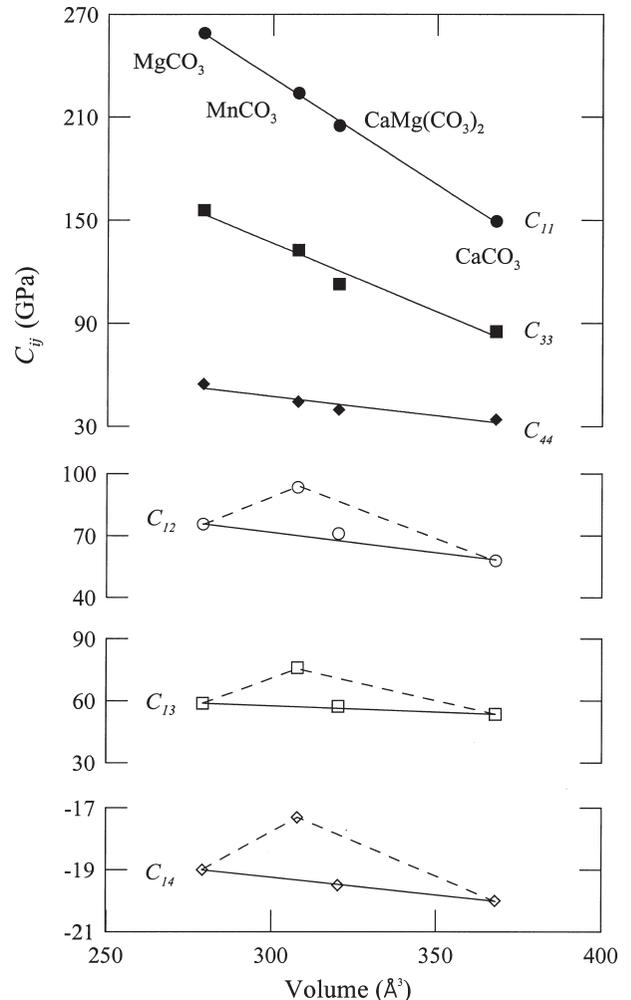
	$C_{11}$	$C_{33}$	$C_{44}$	$C_{12}$	$C_{13}$	$C_{14}$	$K_{\text{VRH}}$	$G_{\text{VRH}}$
Hearmon (1979)	259	156	54.8	75.6	58.8	-19.0	114.0	68.0
<b>magnesite (<math>\text{MgCO}_3</math>)</b>								
This work*	223.9 (15)	132.6 (41)	44.5 (9)	93.4 (21)	76.0 (23)	-17.3 (6)	114.3	49.8
<b>dolomite [<math>\text{CaMg}(\text{CO}_3)_2</math>]</b>								
Humbert & Pliquet (1972)	205	112.8	39.8	71	57.4	-19.5	94.8	47.1
<b>calcite (<math>\text{CaCO}_3</math>)</b>								
Danderkar (1968a)	148.0	85.7	32.8	55.4	54.5	-20.8	76.1	31.8
Danderkar (1968b)	146.3	85.3	34.0	59.7	50.8	-20.8	74.7	31.8
Hearmon (1979)	144	84.0	33.5	53.9	51.1	-20.5	73.3	32.0
Vo Thanh & Lacam (1984)	145.7	85.3	33.4	55.9	53.5	-20.5	75.3	31.7
This work*	149.4 (7)	85.2 (18)	34.1 (5)	57.9 (11)	53.5 (9)	-20.0 (2)	76.1	32.8

\* Standard deviations inside parentheses are expressed in units of the last digit. Densities used in this work are 3.720 (Effenberger et al. 1981) and 2.712 (Hearmon 1979)  $\text{g/cm}^3$  for rhodochrosite and calcite, respectively.



**FIGURE 4.** Logarithmic axis ratio  $c/a$  for  $\text{MnCO}_3$  as a function of pressure. Solid and open symbols represent two different experimental runs from Zhang and Reeder (1999). The solid line was based on the elastic constants of  $\text{MnCO}_3$  measured in this study.

rhodochrosite, the same relationship is still valid for the three off-diagonal elastic constants  $C_{12}$ ,  $C_{13}$ , and  $C_{14}$ . These observations suggest that the elastic constants for calcite, dolomite and magnesite could be determined using variables associated with the unit-cell size. The replacement of some Mg by Ca has the effect of increasing the  $V$ , and results in decreasing all six elastic constants. In other words, compositional changes in the three compounds have a secondary effect on the behavior of variations in elastic properties. The behavior of the off-diagonal elements in elastic constants of carbonates cannot be solely attributed to the unit-cell size and thus appears to be most sensitive to the presence of a  $3d$  transition metal cation. We recog-



**FIGURE 5.** Elastic constants  $C_{ij}$  of the calcite-type carbonates as a function of unit-cell volume. Solid symbols are the diagonal elements of the elastic constants and open symbols the off-diagonal elements.

nize that the sample population in this comparison is limited. The effect of 3d transition metal cation in carbonates particularly needs to be studied with additional experiments on other carbonates. A similar effect for the olivine-type silicates (A<sub>2</sub>SiO<sub>4</sub>, A = Ni<sup>2+</sup>, Mg<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>2+</sup>, and Mn<sup>2+</sup>) has been suggested by Weidner et al. (1982) and Bass et al. (1984).

The aggregate elastic moduli for calcite and rhodochrosite calculated using the Voigt-Reuss-Hill (VRH) averaging scheme are also given in Table 1, in which the literature data are also listed for comparison. The off-diagonal elements of the elastic constants are critical in defining aggregate properties, as the Voigt bounds of the aggregate elastic moduli for trigonal crystals are given by Watt (1987) as follows:

$$K_v = (2C_{11} + C_{33} + 2C_{12} + 4C_{13}) / 9 \quad (4)$$

and

$$G_v = (7C_{11} + 2C_{33} + 12C_{44} - 5C_{12} - 4C_{13}) / 30 \quad (5)$$

The large values in the off-diagonal elastic constants will tend to increase the bulk modulus  $K_v$  and decrease the shear modulus  $G_v$ . This would account for the difference in the bulk modulus-cell volume relationships between the alkaline-earth carbonates and the 3d transition metal carbonates reported by Zhang and Reeder (1999).

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