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The Compression of α Quartz

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The isothermal cell edge and volume compressions of α quartz were measured to 12-GPa (120 kbar) hydrostatic pressure by using the modified Jamieson technique. Detailed listings are given of the relative volumes of Al, NaF, and NaCl, the pressure indicators, correlated with pressures to 13 GPa. The measured relative cell edges and volumes of α quartz to 12 GPa are combined with the 0.3-GPa elastic moduli data of McSkimin et al. (1965) to give the following relative cell edge and volume fits: $a/a_0 = 1 - 9.815 \times 10^{-3}P + 8.155 \times 10^{-4}P^2 - 7.779 \times 10^{-5}P^3 + 3.288 \times 10^{-6}P^4$; $c/c_0 = 1 - 7.306 \times 10^{-3}P + 7.875 \times 10^{-4}P^2 - 6.685 \times 10^{-5}P^3 + 2.362 \times 10^{-6}P^4$; $u_{st} = 3.7437 + 1.825u_{pt} - 0.152u_{pt}^2$, $u_{pt} < 0.5$ km/s; and $u_{st} = 3.856 + 1.509u_{pt}$, $u_{pt} > 0.5$ km/s. Here $V/V_0 = (u_{st} - u_{pt})/u_{st}$, $P = \rho_0 u_{st} u_{pt}$, and $\rho_0 = 2.647$ g/cm³. The equilibrium shock compression Hugoniots calculated from the isothermal compression fits are $u_s = 3.758 + 1.828u_p - 0.131u_p^2$, $u_p < 0.45$ km/s, and $u_s = 3.864 + 1.533u_p$, $u_p > 0.45$ km/s, where u_s is the shock velocity and u_p is the particle or mass velocity behind the shock wave.

The compression of α quartz is of interest because α quartz is a major constituent of crustal rocks. Quartz is also an important piezoelectric crystal used for the measurement of sound speeds in liquids and solids and as a pressure gage in both static and dynamic high-pressure research.

Many studies have been conducted on the compression of α quartz. Some of these are the linear and volume compression studies of *Bridgman* [1925, 1928, 1948*a*, *b*, 1949]; the volume compression studies of *Vaidya et al.* [1973]; the elastic constant measurement of *McSkimin et al.* [1965] and *Thurston et al.* [1966], complemented by the equations of *Thurston* [1967] relating elastic constants to linear compression; the high-pressure X ray diffraction data of *McWhan* [1967]; and the shock compression studies of quartz by *Wackerle* [1962], *Fowles* [1967], and *Graham* [1974]. Recently, the high-pressure X ray diffraction technique of *Jamieson* [1964] was modified [*Halleck and Olinger*, 1974] so that more highly resolved X ray diffraction patterns could be obtained from samples held at hydrostatic pressures as high as 10 GPa (1 GPa = 10 kbar). Here the modified Jamieson technique is applied to resolve the isothermal compression of α quartz better. From the isothermal compression the shock compression of α quartz can then be calculated.

This technique involves pressing an annulus of beryllium 3.5 mm in diameter and 0.2 mm thick with a 0.3-mm-diameter hole at its center between two tungsten carbide Bridgman anvils. The hole is filled with a mixture of powdered α quartz and powdered Al or NaF (the pressure indicators) and a mixture of 4:1 methanol-ethanol that remains hydrostatic to 10 GPa [*Piermarini et al.*, 1973]. A CuKα X ray beam is directed through the annulus, and the diffraction is recorded on a 114.6-mm-diameter cylindrical film surrounding the annulus.

The diffraction patterns of the quartz-aluminum mixture or the quartz-NaF mixture at high pressures exhibited the 100, 101, 110, 102, 111, 211, and 104 diffraction lines of α quartz, with the 200 and the 112 lines being occasionally visible in the Be annulus diffraction bands. The pressure was deduced from the relative volumes V/V_0 of Al and NaF calculated from the 111, 220, and 311 lines of Al and from the 200 and 220 lines of NaF. The pressures correlated with the relative volumes of NaF and Al are discussed later. The high-pressure patterns are corrected for the sample position and for self-absorption. The corrections are based on a comparison of three diffraction patterns of the samples recorded at ambient conditions in the high-pressure apparatus with standard patterns. The standard pattern of α quartz ($a_0 = 4.9135 \pm 0.0003$ Å, $c_0 = 5.4052 \pm 0.0004$ Å, $\rho = 2.6473$ g/cm³) is based on a least squares refinement of a pattern taken by using CuKα radiation and a 114.6-mm-diameter powder camera. The α quartz sample studied is the same as that studied by *Wackerle* [1962]. The Al and NaF standard patterns are from the work by *Swanson and Tatge* [1953] ($a_0 = 4.0494$ and 4.6342 Å, respectively).

This study is a revision of an earlier version in which Al alone was used as the pressure indicator. The Al is from the Fisher Scientific Company and is labeled 'A-559 Al metal, finest powder.' The analysis is 99.4% Al, 0.34% Fe, 0.15% Si, 0.04% Zn, and 0.02% Cu; this is nearly equivalent to Al 1060. The study was repeated, NaF being used as the indicator, and the result for a given quartz compression was that the pressure based on the NaF compression was higher than that taken before. The earlier Al pressure scale [*Olinger and Halleck*, 1975] is based on early and sparse shock compression data for Al 1100 (99% pure). A series of studies was immediately carried out to cross-compare our Al indicator with NaCl. The NaCl pressure scale was taken from the work by *Fritz et al.* [1971]. The result of that study was the following isotherm for Al to 15 GPa:

$$u_{st} = 5.290 + 1.388u_{pt} \qquad \rho_0 = 2.701 \text{ g/cm}^3 \qquad (1)$$

where $P = \rho_0 u_{st} u_{pt}$ and $V/V_0 = (u_{st} - u_{pt})/u_{st}$ (B. Olinger, private communication, 1976). The pressures correlated with the relative volumes of NaF were derived from the study by *Carter* [1973]. Subsequent recalculation of the relative volumes of NaF as a function of pressure at 293°K by W. J. Carter (private communication, 1976) shows that his pressures were several percent too low. His current NaF P correlation is in excellent agreement with the NaF, NaCl P correlation study conducted by *Olinger and Jamieson* [1970]. The relative volume-pressure correlations of all three pressure indicators, Al, NaF, and NaCl, to 13 GPa are listed in Table 1.

The relative cell edge and volume compression data for α quartz are listed in Table 2 along with the corresponding volumes and pressures for Al and NaF. In Figure 1 the data are displayed in terms of a/a_0, c/c_0, and V/V_0 as a function of pressure. Also shown in Figure 1 are the smoothed data of *Bridgman* [1949], *McWhan* [1967], and *Vaidya et al.* [1973] and the calculated relative cell edges and volumes of *Thurston* [1967].

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TABLE 1. Relative Volumes of Al, NaF, and NaCl for Pressures up to 13.0 GPa

P, GPa	V/V_0		
	Al	NaF	NaCl
0.5	0.9935	0.9897	0.9802
1.0	0.9872	0.9800	0.9627
1.5	0.9812	0.9708	0.9469
2.0	0.9753	0.9621	0.9325
2.5	0.9697	0.9537	0.9193
3.0	0.9642	0.9459	0.9070
3.5	0.9588	0.9383	0.8957
4.0	0.9537	0.9311	0.8851
4.5	0.9486	0.9241	0.8751
5.0	0.9438	0.9175	0.8657
5.5	0.9390	0.9110	0.8568
6.0	0.9344	0.9049	0.8483
6.5	0.9299	0.8989	0.8403
7.0	0.9255	0.8932	0.8326
7.5	0.9213	0.8876	0.8253
8.0	0.9171	0.8822	0.8182
8.5	0.9130	0.8770	0.8115
9.0	0.9091	0.8719	0.8050
9.5	0.9052	0.8670	0.7987
10.0	0.9014	0.8623	0.7927
10.5	0.8977	0.8576	0.7869
11.0	0.8941	0.8531	0.7812
11.5	0.8906	0.8488	0.7758
12.0	0.8871	0.8445	0.7705
12.5	0.8837	0.8403	0.7654
13.0	0.8804	0.8363	0.7604

The 1949 work by Bridgman was his last on quartz and presumably his most accurate. These data of Bridgman were further corrected by *Rotter and Smith* [1966], and the correction is included here. The linear and volume compression data of Bridgman appear to agree well with our data. *McWhan*'s [1967] technique is similar to ours, except that the environment of the sample is not hydrostatic. The internal pressure gage used by McWhan was NaCl. The pressure scale that we used to convert McWhan's NaCl compressions to pressure was that of *Fritz et al.* [1971]. In Figure 1 the effect of pressure on the c cell edge measured by McWhan appears to agree with that of Bridgman and the present data, but McWhan's data show the a cell edge to be less compressible than was found by either us or Bridgman. Consequently, the volume change reported by McWhan is less than that found by Bridgman or the present study. *Thurston* [1967] calculated the cell edge compressions of α quartz using the second- and third-order elastic constants determined by *McSkimin et al.* [1965] and *Thurston et al.* [1966] to 0.3 GPa. Thurston's results agree well with ours and those of *Bridgman* [1949] (corrected by *Rotter and Smith* [1966]) up to the limit of Bridgman's pressure range, 3 GPa. But above that, the calculated compressions deviate from our data to lower values and eventually fall below McWhan's results. The relative volumes measured by *Vaidya et al.* [1973] show α quartz to be more compressible than do any of the other determinations.

The cell edge compression of quartz can probably be best represented by a combination of the elastic constant measurements of *McSkimin et al.* [1965] and *Thurston et al.* [1966] and the hydrostatic measurements presented here. Thurston's calculated quadratic equations for the relative cell edges using McSkimin's data are

$$a/a_0 = 1 - 9.815 \times 10^{-3}P + 8.155 \times 10^{-4}P^2 \quad (2)$$

$$c/c_0 = 1 - 7.306 \times 10^{-3}P + 7.875 \times 10^{-4}P^2 \quad (3)$$

Here we directly measured the cell edges from 3.0 to 12.0 GPa. The quadratic fits to those data are

$$a/a_0 = 1 - 8.415 \times 10^{-3}P + 2.27 \times 10^{-4}P^2 \quad (4)$$

$$c/c_0 = 1 - 5.964 \times 10^{-3}P + 2.29 \times 10^{-4}P^2 \quad (5)$$

In order to fit the high-pressure cell edge data and yet to reflect the low-pressure compression of α quartz we used the coefficients calculated by *Thurston* [1967] and refit the present data with fourth-order equations

$$a/a_0 = 1 - 9.815 \times 10^{-3}P + 8.155 \times 10^{-4}P^2 - 7.779 \times 10^{-5}P^3 + 3.288 \times 10^{-6}P^4 \quad (6)$$

$$c/c_0 = 1 - 7.306 \times 10^{-3}P + 7.875 \times 10^{-4}P^2 - 6.685 \times 10^{-5}P^3 + 2.362 \times 10^{-6}P^4 \quad (7)$$

These two expressions represent the relative cell edge values of

TABLE 2. Relative Cell Edges, Volumes, and u_{st}, u_{pt} Values for α Quartz to 12 GPa (120 kbar) at 293°K

Pressure Indicator			Quartz				
Type	V/V_0*	P,† GPa	a/a_0*	c/c_0*	V/V_0*	u_{pt},‡ km/s	u_{st},‡ km/s
Al	0.9601 (11)	3.38 (0.09)	0.9733 (3)	0.9827 (4)	0.9309 (7)	0.279 (4)	4.299 (62)
NaF	0.9191 (14)	4.88 (0.10)	0.9651 (5)	0.9745 (10)	0.9076 (14)	0.413 (5)	4.467 (57)
NaF	0.9176 (10)	4.99 (0.07)	0.9646 (3)	0.9761 (5)	0.9083 (7)	0.416 (3)	4.534 (36)
Al	0.9351 (08)	5.92 (0.08)	0.9569 (3)	0.9733 (4)	0.8912 (7)	0.493 (4)	4.534 (34)
Al	0.9289 (12)	6.61 (0.12)	0.9533 (5)	0.9714 (4)	0.8829 (10)	0.541 (5)	4.617 (46)
Al	0.9285 (03)	6.65 (0.05)	0.9546 (2)	0.9706 (2)	0.8844 (4)	0.539 (2)	4.662 (19)
NaF	0.8882 (12)	7.55 (0.10)	0.9513 (4)	0.9686 (6)	0.8765 (9)	0.593 (5)	4.806 (37)
NaF	0.8784 (09)	8.36 (0.10)	0.9461 (3)	0.9658 (4)	0.8646 (6)	0.654 (4)	4.829 (31)
NaF	0.8707 (07)	9.12 (0.07)	0.9434 (5)	0.9647 (11)	0.8586 (14)	0.698 (4)	4.936 (31)
NaF	0.8652 (11)	9.69 (0.11)	0.9402 (3)	0.9646 (5)	0.8526 (7)	0.734 (5)	4.983 (36)
Al	0.9038 (15)	9.69 (0.19)	0.9398 (7)	0.9644 (7)	0.8517 (14)	0.737 (8)	4.968 (54)
Al	0.9001 (17)	10.18 (0.21)	0.9374 (5)	0.9627 (5)	0.8459 (10)	0.770 (8)	4.996 (54)
NaF	0.8603 (08)	10.21 (0.09)	0.9371 (3)	0.9634 (4)	0.8460 (7)	0.771 (4)	5.003 (25)
Al	0.8935 (10)	11.09 (0.14)	0.9336 (5)	0.9612 (5)	0.8378 (10)	0.824 (6)	5.083 (36)
Al	0.8866 (16)	12.07 (0.20)	0.9308 (6)	0.9603 (6)	0.8320 (11)	0.875 (8)	5.210 (47)

*Values in parentheses are the standard deviations times 10^4.
†Values in parentheses are the average deviations.
‡Values in parentheses are the standard deviations times 10^3.

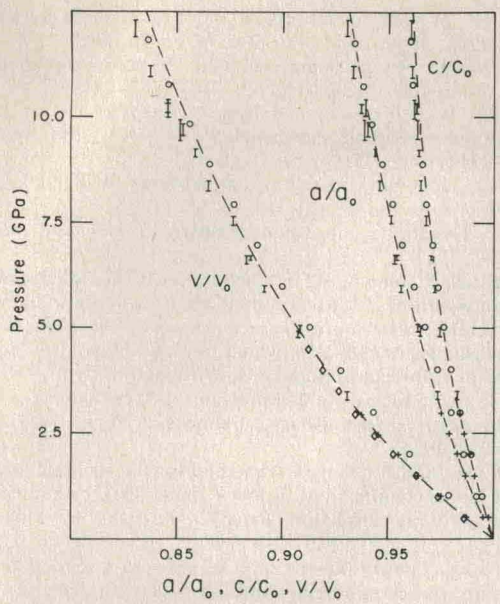


Fig. 1. Effect of pressure on the relative cell edges and volume of α quartz. The vertical bars are the present data; most of the uncertainty is in the pressure. The pluses are the corrected data of *Bridgman* [1949], the diamonds are the data of *Vaidya et al.* [1973], the circles are the smoothed data of *McWhan* [1967], and the dashed curves are the calculated compressions of *Thurston* [1967] based on the data of *McSkimin et al.* [1965].

α quartz only over the pressure range studied here, 12 GPa.

A sensitive means of analyzing the volume compression data is in terms of $[PV_0/(1 - V/V_0)]^{1/2}$ and $[PV_0(1 - V/V_0)]^{1/2}$. For isothermal compression these parameters are linearly related within the resolution of the data for metallic and covalent bonded solids [*Olinger and Halleck*, 1975]. For ionic bonded solids there is a slight curvature at low pressures (J. N. Fritz, private communication, 1976), and for van der Waals bonded solids there is a large curvature at low pressures until the bonds collapse to covalent bondlike distances [*Olinger et al.*, 1975]. The same P, V parameters along the shock compression Hugoniot are the shock wave velocity u_s and the particle or mass velocity u_p behind the shock wave. The relation between these velocities is also usually linear. For isothermal compression we will refer to the parameters as the isothermal shock velocity u_{st} and the isothermal particle velocity u_{pt}, respectively. As was shown earlier [*Olinger and Halleck*, 1975], the value of u_{st} for $u_{pt} = 0$ is the isothermal bulk sound speed c_t, and the initial slope s_t ($\partial u_{st}/\partial u_{pt}$ at $u_{pt} = 0$) can be directly related to the pressure derivative of the zero-pressure isothermal bulk modulus ($B_{0t}' = 4s_t - 1$). Constant slope does not mean that $B_t'(P)$ is constant [see *Ruoff*, 1967].

The present data are shown in Figure 2 along with linear fits to the data of *Bridgman* [1949] (corrected by *Rotter and Smith* [1966]), *Vaidya et al.* [1973], *McWhan* [1967], and *Thurston* [1967]. Only the data of McWhan having u_{pt} values greater than 0.2 km/s were used to determine the fit. McWhan's data having u_{pt} values lower than 0.2 km/s have large scatter. The fit to the selected McWhan data is

$$u_{st} = 4.26 + 1.09u_{pt} \quad (8)$$

The fit to the Bridgman data is

$$u_{st} = 3.69 + 1.90u_{pt} \quad (9)$$

The fit to the Vaidya data is

$$u_{st} = 3.636 + 1.96u_{pt} \quad (10)$$

The linear fit to our data is

$$u_{st} = 3.856 + 1.509u_{pt} \quad (11)$$

A similar fit can be made from the elastic moduli of *McSkimin et al.* [1965] if we assume that the isothermal pressure derivative of the isothermal bulk modulus is the same as that for the adiabatic bulk modulus ($B_{0s}' = 6.3$). That linear fit is

$$u_{st} = 3.7437 + 1.825u_{pt} \quad (12)$$

Of the five static compression studies discussed here the data of *McSkimin et al.* [1965], *Bridgman* [1949], and the present study were gathered from a hydrostatic environment. Those of *Vaidya et al.* [1973] were measured in a low-shear medium. The pressure in the sample cell of McWhan was not hydrostatic [see *Jamieson and Olinger*, 1971; *Piermarini et al.*, 1973; *Singh and Kennedy*, 1974], and this probably accounts for the substantial disagreement between the fit to his data, equation (8), and the fits to the data of the others, equations (9), (10), (11), and (12). Agreement among the remaining compression studies is good to the limits of each pressure range: *Bridgman* [1949], 3 GPa; *McSkimin et al.* [1965], 0.3 GPa; *Vaidya et al.* [1973], 4.5 GPa; and the present study 12 GPa. This agreement is illustrated in Figure 2 to u_{pt} values of 0.35 km/s. The extrapolated compression values of the three former studies diverge from the results of this study. Again, we feel that the low-pressure volume compression of α quartz is best represented by the elastic moduli and their pressure derivatives as measured by *McSkimin et al.* [1965] and *Thurston et al.* [1966]. Using the linear expression derived from their data, equation (12), we refit our data with a quadratic u_{st}, u_{pt} equation. It is this expression (equation (13)) that we feel best represents the compression of α quartz below 6 GPa:

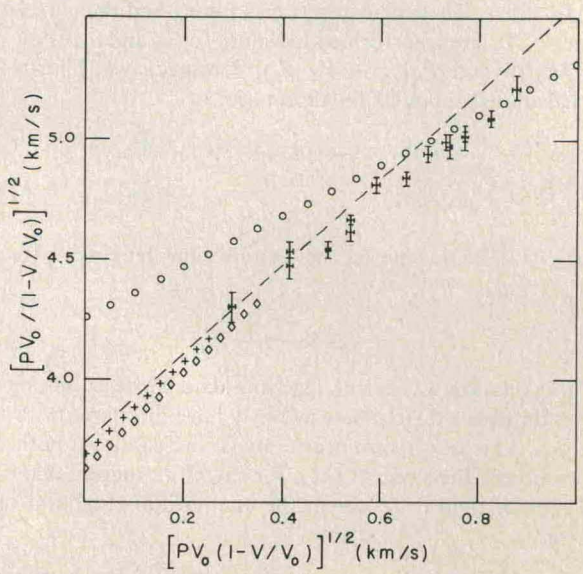


Fig. 2. Volume compression fits and data in terms of $[PV_0/(1 - V/V_0)]^{1/2}$ and $[PV_0(1 - V/V_0)]^{1/2}$. The crossed bars are the present data representing their uncertainty. The pluses are the data of *Bridgman* [1949], the diamonds are the data of *Vaidya et al.* [1973], the circles are the smoothed data of *McWhan* [1967], and the dashed line is the calculated compression based on the elastic moduli of *McSkimin et al.* [1965].

$$u_{st} = 3.7437 + 1.825u_{pt} - 0.152u_{pt}^2 \qquad u_{pt} < 0.5 \text{ km/s} \quad (13)$$

and (11) represents the compression above 6 GPa.

The elastic strength of α quartz has made the measurement of its equilibrium shock compression Hugoniot difficult, but from the isothermal compression of α quartz defined here the Hugoniot can be readily calculated.

The pressure along the Hugoniot, P_h, at volume V_L can be expressed in terms of the pressure along the isotherm, P_t [*Olinger et al.*, 1975]:

$$P_h\{V_L\} = \left\{P_t\{V_L\}(V/\gamma) + \int_{V_0}^{V_L} P\,dV - [(T\gamma/V)C_v](V_L - V_0)\right\} \Big/ [(V/\gamma) - \tfrac{1}{2}(V_0 - V_L)] \quad (14)$$

Here γ is the Grüneisen constant

$$\gamma = \alpha_v c_s^2/C_p \quad (15)$$

where α_v is the volume thermal expansion (3.66×10^{-5}/°K) [*McSkimin et al.*, 1965], c_s is the adiabatic sound speed (3.758 km/s) [*McSkimin et al.*, 1965], and C_p is the heat capacity at constant pressure (7.41×10^{-4} GPa cm³/°K g) [*McSkimin et al.*, 1965]. C_v is the heat capacity at constant volume,

$$C_v = C_p - \alpha_v^2 T c_t^2 \quad (16)$$

Here we assume that C_v (7.35×10^{-4} GPa cm³/°K g) and γ/V (1.854 g/cm³) both remain constant [*McQueen et al.*, 1967]. The integral in (14) is solved by numerical integration:

$$\int_{V_0}^{V_L} P\,dV = \sum_{r=1}^{L} \frac{P_r - P_{r-1}}{2}(V_r - V_{r-1}) \quad (17)$$

where

$$V_r = V_0(u_{str} - u_{ptr})/u_{str} \quad (18)$$

and

$$P_r = (1/V_0)u_{str}u_{ptr} \quad (19)$$

The u_{str}, u_{ptr} values are from (10) and (12) in intervals of $\Delta u_{pt} = 0.01$ km/s. The calculated values for P_h and the correlated values of V_L are transformed to values for u_s and u_p, $[P_h V_0/(1 - V_L/V_0)]^{1/2}$ and $[P_h V_0(1 - V_L/V_0)]^{1/2}$, respectively. The fits for the calculated shock compression are

$$u_s = 3.758 + 1.828u_p - 0.131u_p^2 \qquad u_p < 0.45 \text{ km/s} \quad (20)$$

$$u_s = 3.864 + 1.533u_p \qquad u_p > 0.45 \text{ km/s} \quad (21)$$

Wackerle [1962] reports the equilibrium Hugoniot for α quartz to be

$$u_s = 3.68 + 2.12u_p \quad (22)$$

but this relation was calculated from data clustered in one u_s, u_p region where the elastic wave may have interfered with the analysis. This results in uncertainty in the values of both the intercept and the slope of (22). We therefore suggest that (20) and (21) be used to represent the equilibrium Hugoniot of α quartz.

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