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Effect of High-Low Quartz Transition on Compressional and Shear Wave Velocities in Rocks Under High Pressure

H. Kern

Mineralogisch-Petrographisches Institut der Universität Kiel,
Olshausenstr. 40–60, 2300 Kiel (Germany) F.R.G.

Abstract. The compressional and shear wave velocities in quarzite, granite, and granulite are determined at a fixed confining pressure of 2 kb as a function of temperature up to 720° C. The high-low quartz transition of the constituent quartz minerals is associated with a pronounced decrease in velocity of the compressional waves when approaching the transition and with a significant velocity increase after the transition. In contrast, the effect of the α-β transition on shear wave velocities is small. The drop of V_P is explained by the elastic softening of structure of the constituent quartz minerals near the α-β transition and the opening of grain-boundary cracks, caused by the very high volumetric thermal expansion of the quartz relative to the other component minerals. The velocity increase in the β-field may be attributed to an elastic hardening of the quartz structure. Poisson ratios computed from the velocity data are anomalous for a solid: they become negative within the transition regime. The transition temperature, as indicated by the minimum velocities, is higher in the polycristalline rocks than is expected on grounds of single crystal behavior, and the discrepancy is more marked in granite than in quartzite. The shift of the transition temperature to higher values is explained by internal stresses that arise from the anisotropy of the thermal expansion and compressibility of individual grains and the differences in thermal expansion and compressibility between different component minerals. The role of the α-β quartz transition as a possible cause of low-velocity layers is discussed.

Introduction

Numerous solid-solid phase transitions are known to occur in the earth's interior. It is therefore of prime petrological and geophysical interest to know their effect on the propagation of seismic waves. Kern (1978) observed anomalous behavior of compressional wave velocities in quartz-bearing rocks at temperatures at which the high-low transition in the constituent quartz crystals may

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be expected. The measurements carried out under isobaric conditions gave velocity-temperature curves characterized by a deep velocity-'valley'. The anomaly of wave velocity was attributed to the α-β transition of quartz in these rocks. This paper presents an experimental investigation of this topic performed on quartz single crystals, on quartzite, granite, and granulite in order to clarify the effects of phase transitions on elastic wave velocities.

Experimental Procedure

The seismic velocities have been measured with the ultrasonic pulse transmission method in a 200-ton cubic pressure apparatus. Some particulars of the device can be found in the paper by Kern and Fakhimi (1975).

Compressional and shear waves were generated, respectively, by means of 2 MHz barium titanate and AC-cut quartz transducers. The experiments on quartzite, granite and granulite were carried out on 43-mm cubes. Measurements of compressional wave velocity V_P have been made simultaneously in the three orthogonal directions of the sample cubes to obtain information on the directional dependence of wave velocities. Concurrent measurements of V_P and the shear wave velocity V_S were carried out in one direction. Measurements on quartz single crystals were performed on cylindric samples with a modified solid media pressure technique.

The travel time was determined by comparing, on a dual-trace oscilloscope, the output and input impulses. Velocities are assumed to be accurate within 1%. Good signals could be obtained consistently only above 0.2 kb. Velocities were recorded at about 0.5 kb intervals for increasing pressure and at about 50° C intervals at increasing temperature. To assure that the samples had reached pressure and temperature equilibrium, time intervals of at least 30–40 min between successive readings were allowed.

Specimens

Cubes of 43 mm edge length were cut out of large blocks of quartzite, granite, and granulite macroscopically free of fractures and secondary alteration. The faces of the cubes were ground parallel within 10^{-3} cm. The samples of the quartz single crystals were in form of cylinders about 14 mm in diameter and 26 mm in length. Two samples had the cylinder axis parallel to the *c*-axis, and the other two were cored normal to *c*.

Except for the quartzite, the rocks used for this study were described previously (Kern, 1978). Localities, densities, and modal analyses are given in Table 1.

The essential features of rock fabrics are as follows:

The *quartzite (No. 1419)* consists of xenoblastic grains with approximately the same size.

The *granite (No. 876)* shows an inequigranular texture and the frequency distribution of grain sizes is somewhat seriate. The grain boundary relationships are interlobate.

Table 1. Description of rocks

No.	Rock	Density (g/cm^3)	Grain size (mm)[a]		Modal analysis (vol %)
			length	width	
1419	quartzite, Koli, Finland	2.662		0.2–0.6	100 qu
876	granite, source unknown	2.653	0.5–1.0	0.4–0.9	33.1 or (microcline); 30.8 plag (19 an) 21.6 qu; 13.5 bio; 1.0 chl
154	granulite, Inari, Finland	2.624	2–3	0.3–0.5	61.6 or (20 ab, 77 or, 3 an); 28.2 qu; 6.3 plag (24 an); 1.9 sill; 2.0 gar (62 alm, 1 spess, 5 gross, 1 andr, 31 pyr)

plag: plagioclase; *or:* orthoclase; *qu:* quartz; *gar:* garnet; *bio:* biotite; *chl:* chlorite; *sill:* sillimanite

[a] Average diameters of the predominant minerals

The *granulite (No. 154)* exhibits an inequigranular texture with a distinct bimodal frequency distribution of grain sizes. Platelike and flaserlike granoblasts of quartz and – to a lesser extent – of orthoclase occur in a finer-grained matrix of more or less equigranular, polygonal orthoclase and plagioclase. The quartz-granoblasts consist of several crystals with lattice orientation differing only slightly, thus indicating sub-grain structures. Preferred orientation of minerals was determined by X-ray goniometer (quartzite) and by universal stage measurements (granite, granulite).

The pole-figures (not reported) for the $(10\bar{1}1)$- and $(11\bar{2}0)$-planes indicate only a weak preferred orientation of quartz c-axes in the quartzite. In the granite the lattice orientation of minerals is random. In the granulite the quartz granoblasts show a weak preferred lattice orientation in spite of the very strong preferred dimensional orientation.

Results

Compressional and Shear Wave Velocities

Compressional wave velocities of the polycrystalline quartzite, granite, and granulite are presented as simple averages of the three orthogonal directions of the sample cubes. A correction due to the change of the length of the specimens with pressure and temperature, respectively, was applied to the calculation of velocity, except for the quartz single crystals.

Figure 1a presents the compressional wave velocities as a function of temperature at a fixed confining pressure of 2 kb for the three quartz-bearing rocks under study. The velocities fall within a relatively short range of temperature and rise again with temperature. As was suggested earlier (Kern, 1978), the discontinuous change of V_P at a definite temperature may be associated with

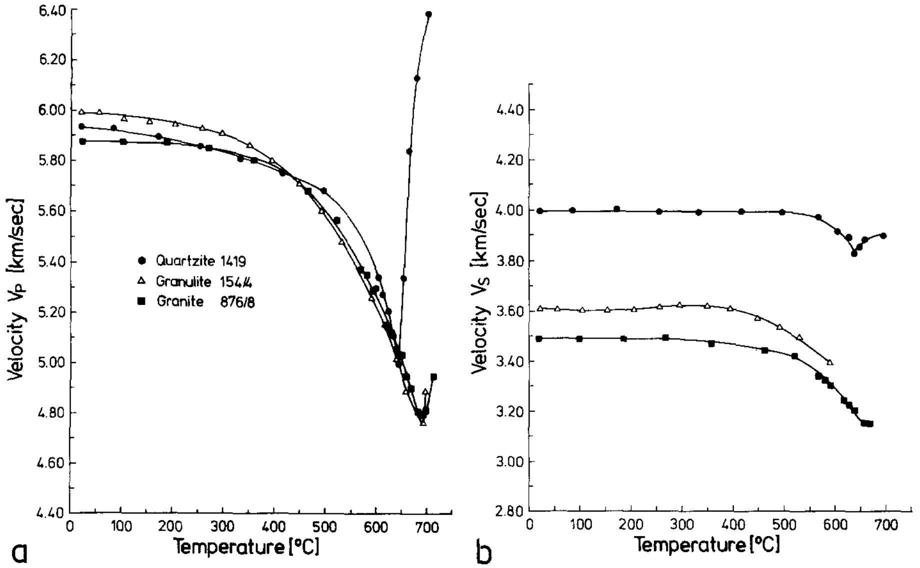


Fig. 1a and b. Compressional wave velocities V_P (**a**) and shear wave velocities V_S (**b**) as a function of temperature at 2 kb confining pressure in quartizite, granite, and granulite

the high–low structural transition of the constituent quartz crystals in these rocks. Further interesting features are revealed by the velocity–temperature relations.

1. The velocity versus temperature curve of granite is similar to that of granulite. The minimum velocity occurs at temperatures of about $695 \pm 5°$ C. In contrast, the minimum velocity in quartzite is found at about $645 \pm 5°$ C.

2. The amount of velocity drop near the α-β quartz transition seems to be independent of the content of the constituent quartz crystals. The velocity drop in the granite and granulite (21.6 vol % and 28.2 vol % quartz, respectively) compares with that of quartzite (100 vol % quartz). However, the velocity-'valley' is much broader in the granite and the granulite than in the quartzite.

3. The transition temperature at a fixed confining pressure seems to be influenced by the component minerals.

The corresponding diagram of shear velocities is shown in Figure 1b. For the granite and granulite specimens the first arrival of *S*-waves became so weak near and above the transition temperature that a determination of the arrival time was not successful. However, fairly good signals were obtained in the quartzite. The transition temperature in the quartzite compares with that indicated by the minimum velocities of compressional waves.

Comparison of V_P and V_S reveals that the high–low quartz transition has an appreciable effect on compressional wave velocities, whereas the effect on shear wave velocities is only small, thus leading to very low values of the V_P/V_S-ratio with increasing temperature.

Earlier measurements (Kern, 1978) demonstrated that the transition temperatures indicated by the minimum velocities are shifted to higher temperatures as confining pressure is raised, probably as a consequence of the pressure depen-

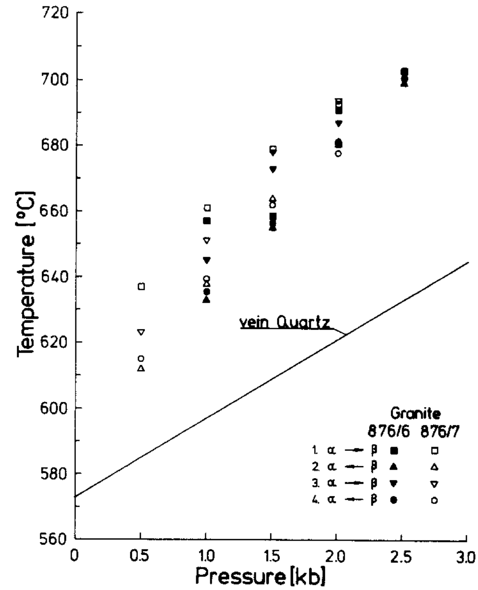


Fig. 2. $T_{\alpha \rightleftharpoons \beta}$ in vein quartz, obtained by DTA technique (van Groos and Heege, 1973) and in polycristalline rock, obtained by V_P-measurements, respectively

dence of the high–low quartz transition. However, the transition temperature at a given confining pressure did not exhibit the same value as obtained by differential thermal analysis on quartz single crystals (van Groos and Hege, 1973). $T_{\alpha \rightleftharpoons \beta}$ in the polycrystalline material measured by ultrasonic technique is generally higher.

To provide more experimental data to reveal the causes for these discrepancies, further experiments were carried out on two samples of granite (No. 876/6-7). The measurements were generally conducted in the following way. Pressure was first raised to about 2.5 kb by steps of about 0.2 kb. The sample cube was then heated within 7 h at a constant rate up to about 580° C. After waiting for equalization of temperature for at least 1 h, temperature was raised in steps of 10°–15° C. During this part of experiment 40–60 min were spent on each measurement. Travel time was measured three times or more. Reproducibility of travel time indicated temperature equilibrium in the sample. Having passed the transition temperature, wave velocities were measured on the way to lower temperatures. On both samples each cycle was repeated. Afterwards pressure was lowered in steps of 0.5 kb and the measurements were done in the same way at confining pressure of 2.0, 1.5, 1.0, and 0.5 kb.

The results are given in Figure 2. From the diagram it is clear that on the way down in temperature the transition appears at lower temperature. Pronounced hysteresis thus appears in the velocity profile. In general the hysteresis is smallest at high confining pressure, and in the second cycle.

Elastic Constants

The simultaneous measurement of V_P in the three orthogonal directions of the sample cubes revealed that at pressures of 2 kb velocity anisotropy is less

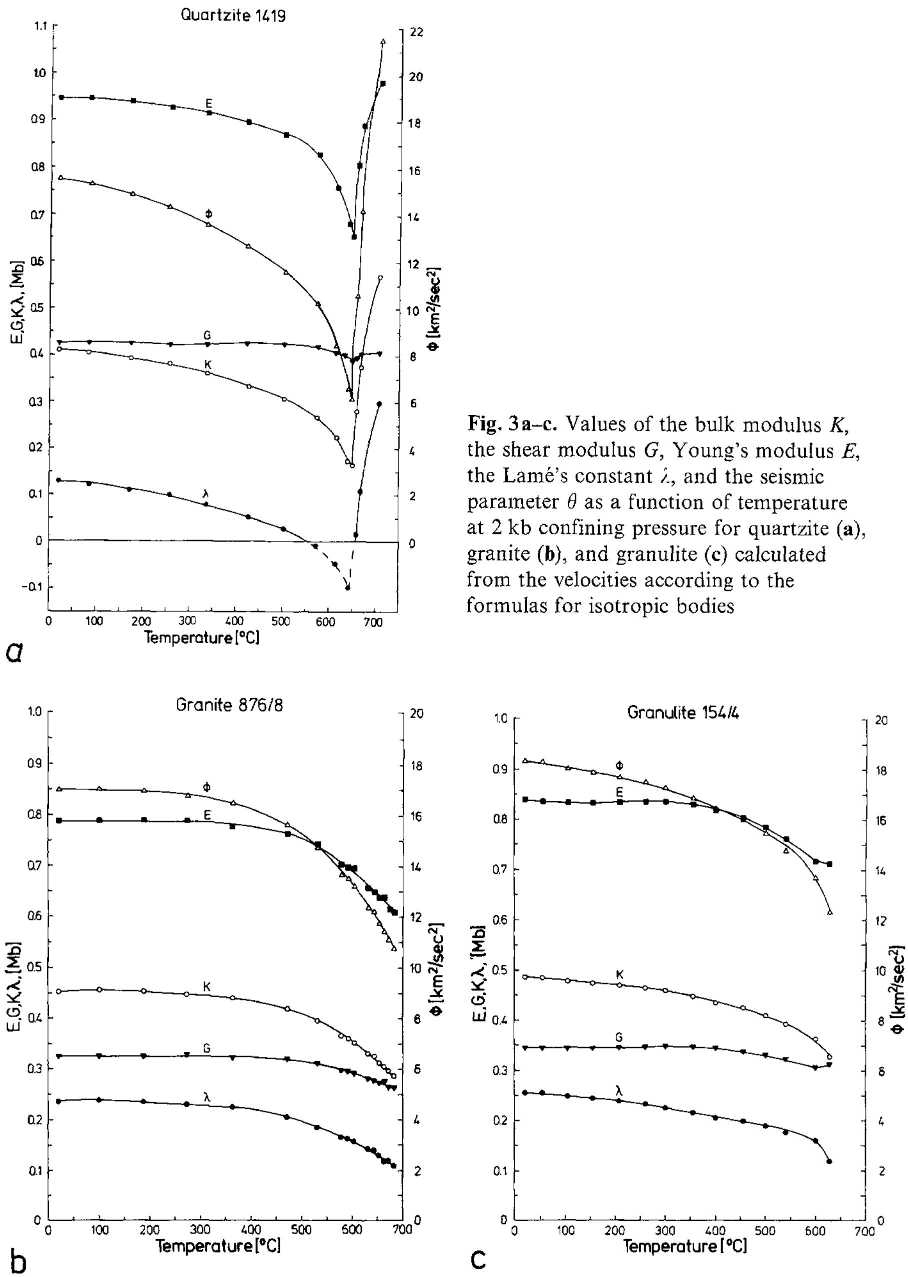
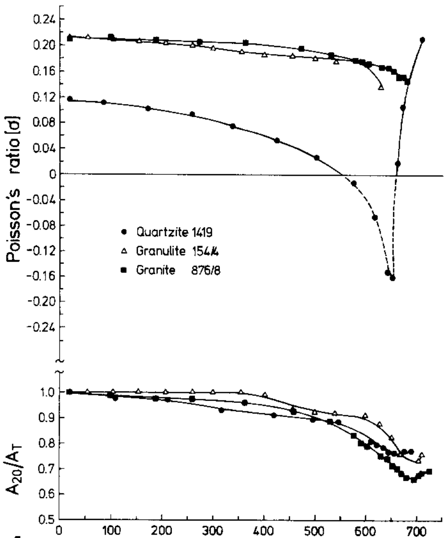


Fig. 3a–c. Values of the bulk modulus K, the shear modulus G, Young's modulus E, the Lamé's constant λ, and the seismic parameter θ as a function of temperature at 2 kb confining pressure for quartzite (**a**), granite (**b**), and granulite (**c**) calculated from the velocities according to the formulas for isotropic bodies

than 1.5%. Thus, it is possible to apply to these rocks the elastic parameters developed for isotropic elastic bodies (Birch, 1960). The concurrent measurement of V_P and V_S permits calculation of all other constants. Values of the bulk modulus K, the shear modulus G, Young's modulus E, the seismic parameter θ, and the Lamé's constant λ at 2 kb confining pressure are given in Figure 3a–c as a function of temperature. It should be noted that the bulk modulus decreases



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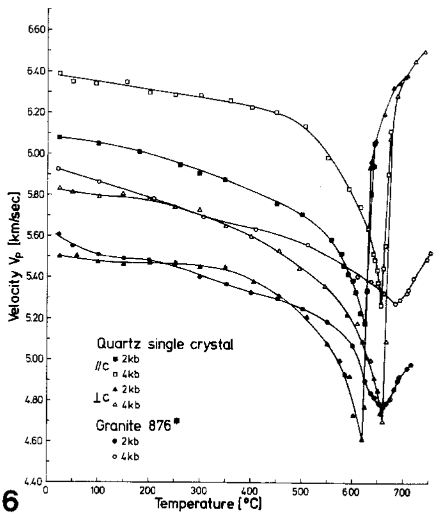

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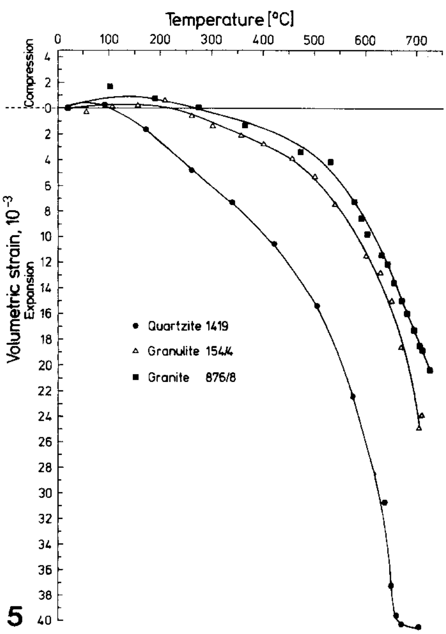

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Fig. 4. Poisson ratio σ and the relative amplitude of *P*-waves A_{20}/A_T as a function of temperature at 2 kb confining pressure

Fig. 5. Volumetric strain (V/V_0) in quartzite, granite, and granulite as a function of temperature at 2 kb confining pressure

Fig. 6. Compressional wave velocities in quartz single crystals and granite as a function of temperature at 2 kb and 4 kb confining pressure, respectively, as measured with a modified solid media technique. Note that the confining pressure calculated from the pressure load on the cross-section of the sample assemblage, may not be strictly identical with the calculated pressure in the cubic pressure apparatus

much more than the shear modulus. Furthermore, it is obvious that the gradual onset of change in slope and the temperature range in which this change takes place corresponds well to the features that appear on the velocity curves. This also holds for E and is especially clear from the diagram of quarzite (Fig. 3a). The most striking feature in Figures 3a and 4, however, is the drastic decrease of the Lamé constant and the Poisson ratio, respectively, with increasing temperature. The constants approach zero at a temperature of about 570° C, and they become negative within the region where the high-low quartz transition takes place. This observation must be attributed to the fact that V_P is very sensitive to the temperature of the high-low transition, whereas V_S is nearly unaffected by that temperature, thus leading to very low V_P/V_S ratios.

Negative Poisson ratios is entirely anomalous for a solid. It implies that it expands in every direction when it is subjected to a uniaxial tension instead of undergoing a lateral contraction. However, Mayer (1960) pointed out that in the case of quartz this anomaly could occur. Also Zubov and Firsova (1962) obtained a negative σ near the α-β transition when measuring the elastic constants of quartz with the Bergmann-Schaefer method.

Volume Change

Thermal volumetric strain as determined from piston displacement is shown in Figure 5. There is a general positive correlation between volume change and velocity decrease with increasing temperature up to the region of the α-β quartz transition. However, the strain curves reveal no positive correlation in the β-field. A significant volumetric discontinuity at the α-β transition was not observed in our experiments. Perhaps it is too minor to be detected with the present type of measurement. Only in the quartzite specimen (100% quartz by volume) may a pronounced change in slope be observed.

Conclusions

Shift of the α-β Transition Temperature

The experiments confirm Kern (1978) that the transition temperature measured in the polycrystalline rocks is generally higher than in quartz single crystals. The difference increases with increasing confining pressure.

From the observations in Figures 1 and 2 it is concluded that the high–low quartz transition in the quartzite is highly influenced by the anisotropy of thermal expansion and compressibility of individual grains, and by the differences in thermal expansion and compressibility between component minerals in granite and granulite. Because of the significantly higher thermal expansion of quartz (Skinner, 1966), it will tend to be under greater compressive stress than the other constituents. This may explain that the α-β transition will be higher than expected, and that the discrepancy is more marked in granite and granulite than in quartzite.

This conclusion is substantiated by V_P measurements on cylindrical samples of quartz single crystals and of granite. The experiments were carried out with a modified solid media technique under the same experimental conditions. Although the absolute pressure, calculated from the pressure load on the cross section of the sample assemblage, may not be comparable with the pressure operating in the experiments with the cubic pressure apparatus, it is clear from Figure 6 that the high–low transition at 2 kb and 4 kb confining pressures occurred in the polycrystalline granite at a higher temperature than in the quartz single crystals.

Wang (1968) and Wang and Meltzer (1973) observed similar anomalities of acoustic wave propagation in marbles and limestones near the calcite 1-calcite 2 transition. They also concluded that inhomogeneous stresses and strains, expected in the neighborhood of pore spaces and angular contacts among grains, may greatly affect the velocity near the transition and cause the maximum velocities to occur at different pressures.

Recently, Coe and Paterson (1969) investigated the effects of nonhydrostatic stress on the α-β quartz transition. They demonstrated that the temperature of the high–low transition in a single crystal of quartz subjected to nonhydrostatic stress depends strongly on the orientation of the crystal with respect to the principal axes of stress: the transition temperature is raised about 10.6° C for each kb of compressive stress perpendicular to the c-axis and only 5° C/kb parallel to c. It must be noticed that the transition did not appear to be significantly smeared by nonuniformities in the specimen. Quartz can withstand large stress differences without breaking. As a consequence of the large thermal expansion of the constituent crystals in the polycrystalline material, stress inhomogeneities may be very large, thus leading to significant variations of the transition temperature.

Causes for the Abnormal Velocity Behavior at the High-Low Transition

Wang (1966, 1968) observed a large drop of the compressional wave velocities in limestones, marbles, and calcite, starting near 15 kb. He showed that the decrease in compressional wave velocities was associated with the calcite 1–calcite 2 transition.

To give an explanation for the velocity drop associated with this transition, Wang (1968) proposed a model based on a mixture of two types of domains, calcite 1 and calcite 2. The domains of the two modifications are considered to have highly mobile boundaries, as is evidenced by the reversibility of the phase transition. With increasing pressure the boundaries move to increase the amount of calcite 2, with decreasing pressure the boundaries would move to decrease it. Under the influence of stress exerted by ultrasonic waves, they may oscillate, giving rise to the abnormal behavior of wave velocities in calcite rocks.

Using similar concepts, Walsh (1973) recently gave a theoretical explanation of the propagation of ultrasonic waves in rocks undergoing polymorphic phase transitions. His analysis demonstrates that the transition can have an appreciable effect on wave velocities and the attenuation of the transmitted energy, if the regions transforming are in the form of thin planar areas. The effect may be large even though the amount of material transformed is very small.

In the case of α-β quartz transition such planar elements could be formed by Dauphiné twins. According to Young (1962, 1964), Dauphiné twinning starts a few degrees below the α-β transition, and continues until the crystal is 'completely' (i.e., 50%) twinned on a microscale.

The question, however, arises whether the mechanism proposed by Wang (1968) and Walsh (1973) is valid generally. The calcite 1–calcite 2 transition is followed by a significant increase of density. In contrast, in quartz a pronounced density decrease is observed when approaching the transition, followed by only a weak increase after the transition. Although the model mentioned above may explain the velocity minimum in the region where the high–low transition proceeds, it does not explain the large velocity increase in the β-field as the temperature is raised, leading to V_P-values appreciably above the velocities measured at room temperature. In the case of quartz single crystals and quartz-bearing rocks, there is no need to explain the drastic decrease of V_P velocities near the transition regime with a special model.

The velocity decrease (cf. also Kern, 1978) strongly correlates with the abnormally high thermal volume expansion of the quartz single crystal (Skinner, 1966) and the quartz-bearing rocks (Fig. 5). The problem is how to explain the significant velocity increase in the β-field.

Following Young (1962, 1964) the rapid reduction of elastic constants, and many other physical properties of α-quartz above about 400° C are at least qualitatively related to a general atomic-force-constant 'softening' due to the increasing anharmonic vibrational character as a consequence of a shift in the atomic equilibrium positions. It is thought that the Si$-$O distance is kept constant and that the shifts take place along directions joining Dauphiné twin-related positions. At or slightly above the transition, the anharmonic vibrational character disappears, giving rise to the 'hardening' of the force-constants and thus leading to higher elastic constants.

High–Low Quartz Transition as a Possible Cause of Low-Velocity Zones

The discontinuous change in compressional and shear wave velocities in the quartz-bearing rocks associated with the high–low transition of the constituent quartz crystals gives rise to the question if the sharp velocity decrease may account for low-velocity zones in the earth's crust in regions with anomalously high heat flow.

As is emphasized by Wang and Meltzer (1973), phase transitions in the earth's interior with characteristic times of about 0.1–1 s or less would affect the propagation of seismic waves, resulting in a pronounced decrease of velocities and a marked increase in attenuation of transmitted energy. On the other hand, it has been concluded recently that partial melting in the presence of traces of water is required to explain channels of low wave velocities (Anderson and Sammis, 1969).

A sensitive parameter to test these two mechanism might be the Poisson ratio and the attenuation of transmitted energy. In Figure 4 the Poisson ratio and the relative amplitude of the first arrival of *P*-waves is plotted against temperature at a constant confining pressure of 2 kb. The Poisson ratios σ shows a sharp decrease in the temperature range where the α-β transition occurs and rises again with temperature, corresponding well with the features that appear on the velocity profile. The amplitude of the first arrival of *P*-waves also decreases near the transition range. A similar decrease of σ and of the amplitude of *P*-waves was observed by Wang and Meltzer (1973) for the pressure-induced calcite 1–calcite 2 transition.

A decrease in σ is generally believed to be characteristic of phase transitions, whereas it may not be expected at the onset of partial melting (Wang and Meltzer, 1973). The P- and S-wave velocity profiles of the earth's interior published so far (Press, 1966; Johnson, 1967; Anderson and Julian, 1969) reveal no obvious changes in the Poisson ratio across the low-velocity zone in the upper mantle. From this observation one might conclude that low velocity layers are not caused by phase transitions. It must be emphasized, however, as a fine structure in the velocity distribution is not available at the present time, that the present picture of low-velocity zones may not be entirely accurate.

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