GEOPHYSICAL RESEARCH LETTERS, VOL. 28, NO. 11, PAGES 2293-2296, JUNE 1, 2001

Observation of anomalous elastic behavior in rock at low temperatures

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Abstract. We have measured qualitative elastic properties of basalt and Berea sandstone from room temperature down to 4 K using Resonant Ultrasound Spectroscopy (RUS). A simple elastic solid should show a monotonic increase in the elastic constants as temperature decreases. The basalt samples show this gross behavior while the sandstone shows a very unexpected anomalous regime between 40 K and 200 K where the elastic constants decrease with decreasing temperature. Both rocks show temperature-dependent structure in both the modulus and internal friction, and also significant hysteresis, indicating history and rate-dependent properties. This data provides insight into the time and energy scales of dynamical effects observed in sandstones. The low temperature range (4K–300K) is of interest due to the renewed interest in Mars and Lunar rocks.

Introduction

Recent work on the acoustic response of rocks to transient mechanical strains demonstrate that rocks may respond nonlinearly [*Meegan et al.*, 1993], hysteretically [*Holcomb*, 1981], and recover logarithmically in time [*Guyer et al.*, 1999]. The authors point out the importance of understanding the dynamics of these systems at a molecular and microstructural level. Processes that may be used to model these slow dynamical and other nonlinear effects, may involve mobile defects or boundaries, or even phase transitions under strain. These should all show a strong temperature dependence, either in the form of an activation or barrier energy or as a change in the form of the free energy.

Low temperature experiments performed on rocks is becoming important as we investigate extraterrestrial environments. Mars and Lunar surfaces, for example, we know to have very dry low temperature environments and surface compositions similar to terrestrial geology. Many of the characteristic energies of phase transitions and mobility freezing for minerals correspond to temperatures well below room temperature, a region not often explored for geological specimens. Also, assuming that low temperatures produce higher strains in rocks, the behavior of rocks at low temperatures can be translated as the behavior of the rocks at high pressures, from a strain point of view.

We have made low temperature acoustic resonance measurements on two samples: a Berea sandstone that has been shown to display hysteretic dynamical properties [*Tencate and Shankland*, 1996], and a Los Alamos basalt. RUS data allows us to determine the qualitative behavior of the elastic constants and the internal friction of a sample. The data show a remarkable difference between these two rock samples, and previous work [*Guyer et al.*, 1999] also suggests that the sandstone has exceptional elastic properties. We observe evidence of characteristic temperatures in both rocks, and a region of anomalous temperature coefficient in the sandstone. The cooling and warming data show hysteresis in both samples, with a significant and repeatable loop apparent in the sandstone. We believe the processes associated with the characteristic temperatures evident in these data are related to the processes that produce the observed [*Tencate and Shankland*, 1996] strain-driven slow dynamics at room temperatures.

RUS, samples, and measurements

Resonant Ultrasound Spectroscopy (RUS) [*Migliori and Sarrao*, 1998] is a technique used to deduce elastic properties from measurements of the low-lying free-vibration modes of a small object. If the object is homogeneous, and of known density, geometry and symmetry, the values of the elastic moduli may be determined with high accuracy. Measurements of the steady-state vibration amplitude are made as a low-amplitude excitation is swept through a range of frequencies. This response amplitude becomes large in the vicinity of a natural resonance frequency of the sample. RUS is particularly well suited to measuring over a wide temperature range, and the resonances of any irregular, or inhomogeneous sample, while not suitable for modulus determination, can yield valuable information on temperature effects. Our samples were cut to approximate rectangular prisms with side dimensions of 3–4 mm and masses near 0.2 g. The basalt sample was collected near Los Alamos, New Mexico; the sandstone sample originated in Berea, Ohio.

The samples are held vertically between diagonal corners by piezoelectric transducers in a RUS cell made for use in a liquid helium cryostat. The sample space was evacuated to 10^{-3} Torr at room temperature and held for several hours to remove as much water as possible, since we expect moisture to have a considerable effect on the elastic properties. The sample space was then backfilled with 1 Torr of He gas to act as a heat transfer medium, and the cryostat was filled with liquid cryogens. The system was allowed to cool to 77 K over about 10 hours, and then to 4 K in a further 3 hours. A spectrum of the resonances in the frequency range 80 kHz to 400 kHz was recorded every 2.5 K. The warm-up

Paper number 2000GL012480.
0094-8276/01/2000GL012480$05.00

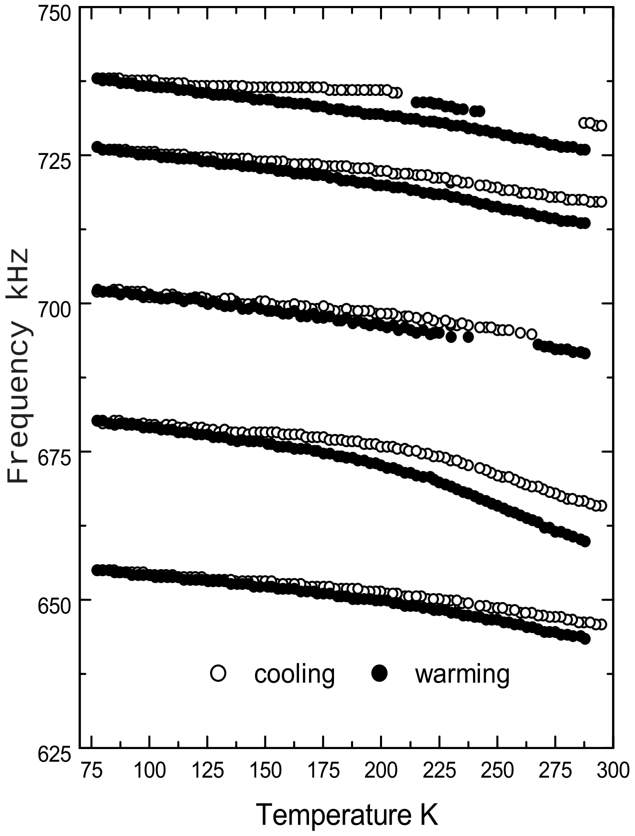

Figure 1. Resonance frequencies for basalt as a function of temperature. The plot is monotonic with a negative temperature coefficient, and shows some deviations from model behavior.

and data rates from 4 K to room temperature were similar; this data allows us to probe for hysteresis. We measure the peak center frequencies and widths. The frequencies are proportional to the square root of the combination of elastic moduli which participate in the motion of the resonance.

Simple models for elastic solids with no phase transitions suggest the temperature dependence of any elastic constant, C, should be a smooth increase as temperature decreases. This temperature dependence is linear at high temperatures and curves at lower temperatures to meet T = 0 K with dC/dT = 0. An experimentally verified empirical expression for this behavior [*Varshni*, 1974] is used as a reference against which we compare our observed elastic behavior. No *a priori* expression is used for comparison with the internal friction data since many possible anelastic processes may contribute. A more detailed analysis will be presented in a future publication [Darling, et al manuscript in preparation, 2001].

Two reliable data may be determined from RUS spectra: the center frequencies of resonance peaks, corresponding to values of the elastic moduli; and the widths of the peaks, corresponding to the internal friction of the modes, and proportional to 1/Q. Widths are determined by fitting a Lorentzian lineshape to the peak. Although we cannot exactly identify the modes of vibration, the lowest resonances are generally dominated by the lowest value shear modulus. Some modes may have a small longitudinal component, yielding a slightly different behavior for those modes.

Results

Basalt

Figure 1 shows the dependence of several basalt resonance peak frequencies on temperature. The data for each resonance are approximately linear (with a small positive curvature) above and below 190 K, with a knee at approximately 190 K. The variation seen in the behavior of the resonance frequencies is due to the different combinations of moduli which contribute to the mode motion. Figure 2(a) and (b) show details of the width and frequency shift of one resonant mode from the sample used in Fig /reffig1. The frequency data deviates from the model behavior by opposite curvatures, a sharper than expected "knee" as the curve flattens, and an obvious hysteresis above 75 K, however the gradient dC/dT is always negative. The width data 2(a), defines three distinct regions which seem well fitted by straight lines, crossing at 141 K and 190 K. Hysteresis is observed in the width only above 190 K.

Sandstone

The sandstone sample, subjected to the same procedure as the basalt shows remarkably different behavior. Several resonance peak frequencies as a function of temperature are shown in Figure 3. As expected, the resonance frequencies increase as the sample is initially cooled. However, between 170 K and 200 K, all three resonance frequencies exhibit a maximum. On further cooling, the resonance frequencies

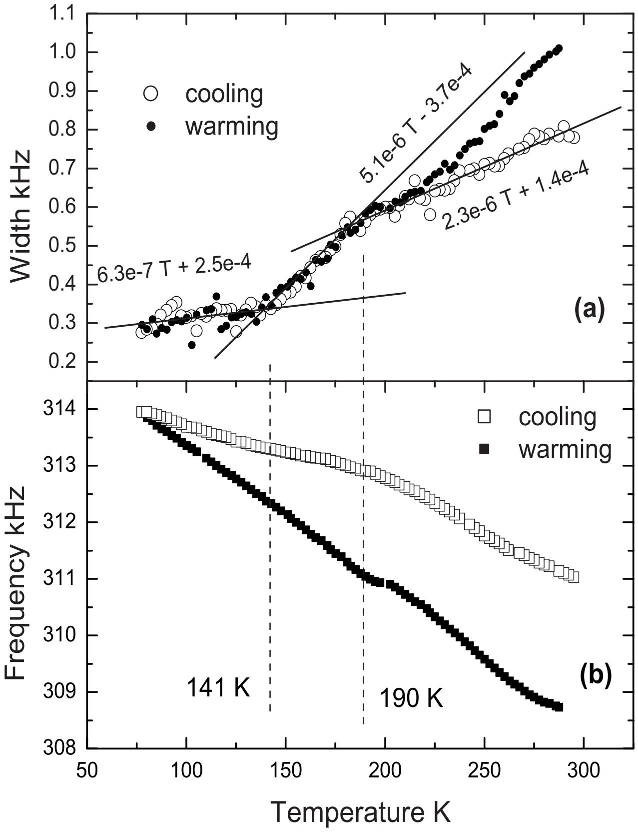

Figure 2. (a) Width of one basalt resonance as a function of temperature, with the gradients of lines which describe sections of the data, (b) the center frequency of the same peak. The line is a "best fit" to a model of a simple solid.

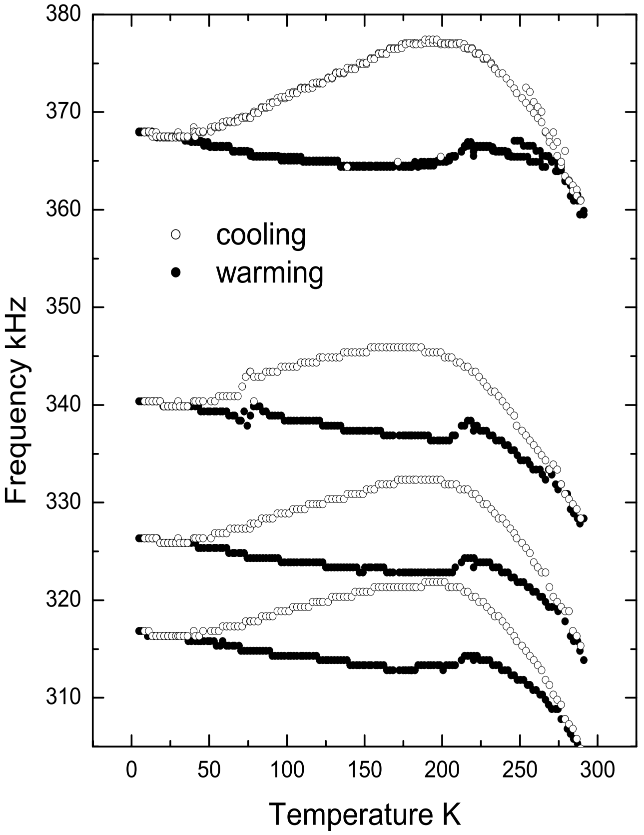

Figure 3. Resonance frequencies for sandstone as a function of temperature. The plot displays both negative and positive temperature coefficients on cooling, and a monotonic negative temperature coefficient on warming. Hysteresis between 40 K and 300 K is apparent.

decrease and gradually flatten to approach 0 K with zero gradient below 60 K, as thermodynamics requires. Thus, on cooling, the sandstone exhibits a positive temperature coefficient between approximately 60 K and 200 K. Positive temperature coefficients are unusual and usually indicate instability. Upon warming, hysteresis is evident in the resonance frequencies above 40 K. The positive temperature coefficient is not recovered in the warming data, as the resonances monotonically decrease. A knee in this data is evident between 200 K and 220 K, however data taken at higher warming rates show no evidence of this and continue smoothly to meet the cooling resonances near 300K. Here, above 220 K, the warming resonances tend towards the cooling resonances, much earlier. The frequency loops are repeatable, with small differences that depend on the maximum temperature probed and the rates involved. The high-rate high-temperature end of the loop may be higher than 300K. Figure 4 (a) and (b) show width and frequency shift for one resonant mode in the sandstone data, taken from the same sample used in fig. 3. In (b) the model function has been fit only in the range above 190 K. The positive temperature coefficient exists between 35 K and 190 K, and the sandstone exists in two distinct elastic states in the range 35 K - 300 K, depending on the history. The width remarkably shows no hysteresis in this range, and follows a curve which can be described by a single exponential function, with a characteristic temperature of 58 K.

Discussion

Recent space exploration studies have focused attention on the compostion of Martian and Lunar surfaces. These studies (NASA Lunar Prospector and Mars Pathfinder projects) have found large quantities of silicates and basaltic rocks, similar to the composition of the terrestrial surface. The atmospheric conditions, however, differ wildly from that found on Earth. Mars has surface temperatures ranging from 140 K to 240 K, while the moon exhibits a more extreme temperature environment with temperatures ranging from 80 K to 380 K. This vast difference in conditions can result in physical properties of the surface materials that are different from expected, based on our knowledge of similar materials here on Earth.

This paper presents qualitative elastic data on the very low temperature behavior of two types of rock. Low temperature analysis is commonplace in materials science where the connection of the elastic moduli to the strain derivatives of the free energy will reveal characteristic temperatures of phase changes by deviations (discontinuities, breaks in slope, changes in Q) from expected behavior. In many martensites, a positive temperature coefficient indicates an elastic instability that leads to a phase transition to a lower free energy structure at lower temperatures. Thermal contraction produces strains which can be equivalent to those produced by hydrostatic pressure. Geological samples are rarely studied at cryogenic temperatures, however the same fundamental

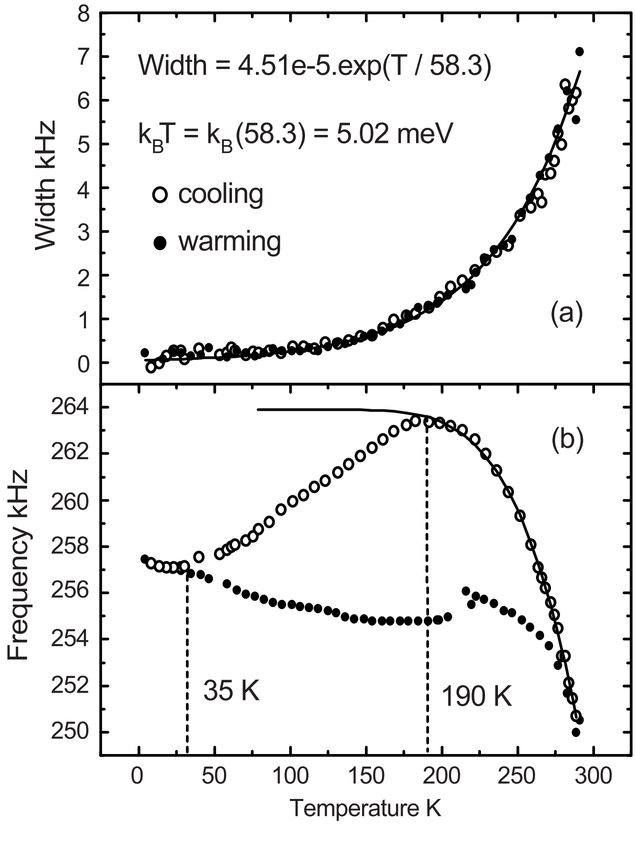

Figure 4. (a) Width of one sandstone resonance as a function of temperature. A single exponential function fits the data and there is no hysteresis, despite the effects visible in (b) the center frequency variation of the same peak. The line is a "best fit" above 190 K to a model of a simple solid.

processes are at work, although complicated by the variety and inhomogeneity of rocks.

The basalt displays hysteresis in the region 75 K - 300 K, but the loop does not close at 300 K at the rates in this measurement. The gross feature of a negative temperature coefficient agrees with a simple model, but the detailed behavior is complex. The internal friction data suggests three linear forms which cross at temperatures of 190 K and 141 K. The change in width is only a factor of 2-3 sharper from 300 K to 75 K, but different dissipation mechanisms may dominate each region.

In Berea sandstone we observe two characteristic temperatures, defining three regions of behavior: (a) 35 K and below, where the material is not hysteretic and displays low internal friction, possibly a region where no defects are mobile, (b) between 35 K and 190 K, where on cooling from T=300 K the material enters a region of instability and an elastic shear modulus becomes softer, while on warming from lower temperatures the behavior is hysteretic, and follows a curve with $dC/dT < 0$, and (c) above 200 K where the cooling behavior shows a model-like hardening of a modulus, but where the warming curve shows a rate-dependent desire to rejoin the cooling curve. It is possible that a third characteristic temperature exists above 300 K which marks the maximum extent of the hysteresis loop. While these temperatures correspond to characteristic energies in this sample, it is not clear whether the three regions define phases or regions of rate-dependent behavior. The simple description of the internal friction suggests that only a single dissipation mechanism is operating, with a characteristic temperature of 58 K and a sharpening of nearly an order of magnitude between 300 K and 77 K, in contrast with the basalt response.

The correlation between the modulus softening and time dependent recovery observed by [*Tencate and Shankland*, 1996] at increasing strains in this sandstone, and the fact that they too see less effect in basalt-like rocks, leads us to believe that our observed temperature dependent behavior is intimately connected to their strain dependent behavior, and is a result of the same fundamental phenomenon. More extensive data and analysis will be presented in a forthcoming publication [Darling, et al manuscript in preparation, 2001].

Acknowledgments. We are grateful to K. R. McCall, P. A. Johnson, J. A. TenCate, R. A. Guyer, and T. J. Shankland for helpful criticism and discussions.

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(Received October 12, 2000; revised January 30, 2001;
accepted February 26, 2001.)