

1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

1.3.4.6. Experimental determination of elastic constants

1.3.4.6.1. Introduction

As mentioned in Section 1.3.4.1, the elastic constants of a material can be obtained by the elastic response of the material to particular static forces; however, such measurements are not precise and the most often used approach nowadays consists of determining the velocity of ultrasonic waves propagating along different directions of the crystal and calculating the elastic constants from the Christoffel determinants (1.3.4.8). The experimental values are often accurate enough to justify the distinction between static and dynamic values of the elastic constants and between phase and group velocities, and the careful consideration of the frequency range of the experiments.

(i) *Static and dynamic elastic constants.* When one measures the elastic response of a material to external static forces, work is done and heat is produced. In general, the external forces are applied slowly (quasi-elastic processes) and the solid body remains in thermal equilibrium with its surroundings, which can be considered as a heat reservoir. In this case, the measured elastic constants are isothermal elastic constants as defined in Section 1.1.5.1. On the contrary, when ultrasonic waves propagate in a solid body, the compressed regions are slightly hotter than the expanded regions; the associated temperature gradients give rise to irreversible processes of thermal conduction. However, in the megahertz or higher-frequency ranges, the processes of heat exchange between different regions or between the solid and its surroundings are slow compared with the period of the ultrasonic wave and hence can be considered as isentropic. In this case, the measured velocities are isentropic and the elastic stiffnesses deduced from them are the adiabatic elastic stiffnesses as defined in Section 1.1.5.4. The differences between isothermal and adiabatic elastic stiffnesses can be calculated from equation (1.1.5.2):

$$\begin{aligned}\delta T_{ij} &= (c_{ijkl})^{\Theta} \delta S_{kl} - \lambda_{ij} \delta \Theta \\ \delta \sigma &= \lambda_{kl} \delta S_{kl} + \frac{\rho C^S}{\Theta} \delta \Theta.\end{aligned}$$

By combining these two equations, it is possible to obtain relations between the isothermal elastic stiffnesses, $(c_{ijkl})^{\Theta}$, and the adiabatic elastic stiffnesses, $(c_{ijkl})^{\sigma}$:

$$(c_{ijkl})^{\sigma} = (c_{ijkl})^{\Theta} + \frac{\lambda_{ij} \lambda_{kl}}{\rho c^S},$$

where c^S is the specific heat at constant strain.

This relation shows that adiabatic elastic stiffnesses are larger than isothermal elastic stiffnesses, at least for the terms of the main diagonal of the elastic matrix. In general, the differences between isothermal and adiabatic elastic stiffnesses are less than 1%. An exception to this statement concerns the temperature region near the critical temperature T_c where a phase transition occurs.

(ii) *Frequency dependence of the elastic constants.* Dynamic measurements of the elastic constants can be performed at a wide range of ultrasonic frequencies. Currently used techniques for investigating a wide range of frequencies are electronic pulse-echo techniques in the megahertz frequency range and Brillouin scattering in the 10 GHz frequency range. To evaluate the possible differences between dynamic elastic constants determined in different frequency ranges, high-accuracy measurements of the *absolute value* of the elastic constants are required. From optical resonance techniques in the megahertz frequency range and Brillouin scattering in the gigahertz frequency range, it has been shown that the results are the same within 0.1 to 0.2% in the case of simple and stable crystals such as sodium chloride when the ultrasonic waves can be considered as a ‘passive probe’ (Michard *et al.*, 1971). Larger differences are observed when ultrasonic waves interact with the medium, when they favour or

impede structural changes of the material or when they are absorbed for a particular frequency.

(iii) *Phase velocity and group velocity.* When the velocity of ultrasonic waves is frequency dependent (dispersive medium), one has to distinguish phase velocity and group velocity. If a resonance technique is used, the resonance frequencies correspond to phase-matching conditions and the calculation of velocity from the resonance frequencies leads to ‘*phase velocity*’. If a pulse-echo technique is used, the transit time of an elastic pulse is measured and the interpretation of the measurement is more complex. In this case, Brillouin (1932) has shown that the head and the tail of the pulse travel with the group velocity. Differences of a few per cent can be observed between phase and group velocities in dispersive media.

1.3.4.6.2. Resonance technique

The use of the resonance technique is a well established approach for determining the velocity of sound in a gas by observing nodes and antinodes of a system of standing waves produced in the so-called *Kund tube*. In the case of transparent solids, optical means allow us to visualize the standing waves and to measure the wavelength directly (Zarembowitch, 1965). An easier procedure can be used: let us consider a transparent crystal in the shape of a parallelepiped (Fig. 1.3.4.1). A piezoelectric transducer is glued to the crystal and excited at varying frequencies. If the bonding between the transducer and the crystal is loose enough, the crystal can be considered as free from stress and the sequence of its resonance frequencies is given by

$$v = nV/2l,$$

where n is an integer, V the phase velocity of the wave in the direction orthogonal to the parallel faces and l the distance between these faces.

The looseness of the bonding can be checked by the regularity of the arithmetic ratio, $V/2l$. On account of the elasto-optic coupling, a phase grating is associated with the elastic standing-wave system and a light beam can be diffracted by this grating. The intensity of the diffraction pattern is maximum when resonance occurs. A large number of resonance frequencies can be detected, usually more than 100, sometimes 1000 for non-attenuating materials. Consequently, in favourable cases the absolute value of the ultrasonic velocity can be determined with an uncertainty less than 10^{-3} .

1.3.4.6.3. Pulse-echo techniques

Pulse-echo techniques are valid for transparent and opaque materials. They are currently used for measuring ultrasonic velocities in solids and can be used in very simple as well as in sophisticated versions according to the required precision (McSkimmin, 1964). In the simplest version (Fig. 1.3.4.2), an electronic pulse generator excites the mechanical vibrations of a piezo-electric transducer glued to one of two plane-parallel faces of a specimen. An ultrasonic pulse whose duration is of the order of a microsecond is generated and transmitted through the specimen. After reflection at the opposite face, it returns and, when it arrives back at the transducer, it gives rise to an electronic signal, or echo. The whole sequence of such echos is displayed on the screen of an oscilloscope and it is possible to measure from them the time interval for transit. Usually, *X*-cut quartz crystals or ferroelectric ceramics are used to excite longitudinal waves and *Y*-cut quartz is used to excite transverse waves. In many cases, a circulator, or gate, is used to protect the receiver from saturation following the main ‘bang’. This method is rough because the beginning and the end of a pulse are not well characterized. Several improvements have therefore been made, mainly based on interferometric techniques (pulse-superposition

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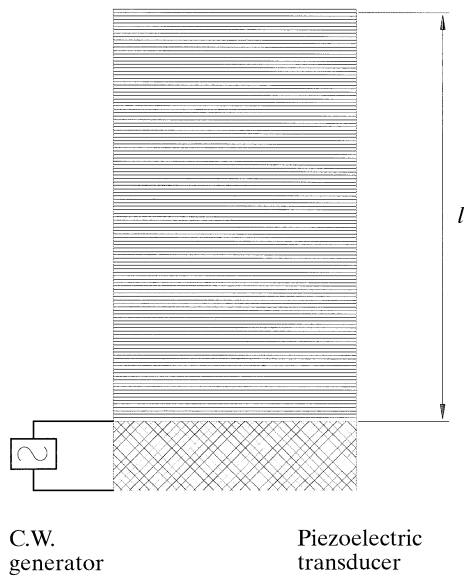


Fig. 1.3.4.1. Resonance technique: standing waves excited in a parallelepiped.

method, 'sing around' method *etc.*). Nevertheless, if the absolute value of the ultrasonic velocity is not determined with a high accuracy by using pulse-echo techniques, this approach has proved valuable when relative values of ultrasonic velocities are needed, *e.g.* temperature and pressure dependences of ultrasonic velocities.

(i) *Pulse-superposition method.* A piezoelectric transducer initiates ultrasonic pulses in the specimen. These pulses echo back and forth within the specimen. A continuous-wave oscillator is used to control the pulse repetition rate. When the repetition rate is adjusted so that the initiation of a pulse coincides with the return of the first echo from the preceding pulses, the change in the signal amplitude indicates superposition. The pulse rate is a measure of the travel time within the specimen.

(ii) *'Sing around method'.* The 'sing around' method for measuring the velocity of ultrasonic waves involves the use of two piezoelectric transducers, one at each end of the specimen. One transducer receives an impulse from the electronic generator and converts it into an ultrasonic pulse in the specimen. This pulse, after passing through the specimen, is detected by the receiving transducer. The received pulse triggers the electronic generator to initiate a succeeding pulse. The pulse repetition rate is a very sensitive probe for measuring changes of the ultrasonic velocity in the specimen. Relative variations of 10^{-7} can be measured, such as temperature or stress dependences of the velocity.

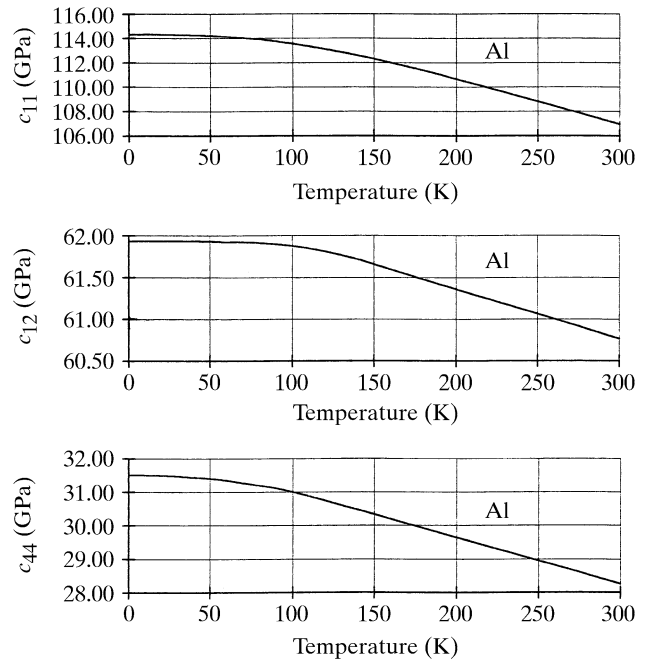


Fig. 1.3.5.1. Temperature dependence of the elastic stiffnesses of an aluminium single crystal (after Landoldt-Börnstein, 1979).

1.3.5. Pressure dependence and temperature dependence of the elastic constants

1.3.5.1. Introduction

In a solid, the elastic constants are temperature and pressure dependent. As examples, the *temperature dependence* of the elastic stiffnesses of an aluminium single crystal within its stability domain (the melting point is 933 K) and the *pressure dependence* of the elastic stiffnesses of the ternary compound $KZnF_3$ within its stability domain (the crystal becomes unstable for a hydrostatic pressure of about 20 GPa) are shown in Figs. 1.3.5.1 and 1.3.5.2, respectively.

We can observe the following trends, which are general for stable crystals:

(i) From 0 K to about $\Theta_D/5$, where Θ_D is the Debye temperature, the elastic stiffnesses decrease according to a Θ^4 law. From $\Theta_D/5$ to the beginning of the instability domain, the dependence is linear with Θ . In addition, $(\partial c_{ii}/\partial \Theta)_p = 0$ at 0 K as predicted by the third principle of thermodynamics.

(ii) For stable crystals, the *pressure dependence* of the elastic stiffnesses is linear as long as the applied pressure is small compared to the elastic stiffnesses. As an example, a typical order

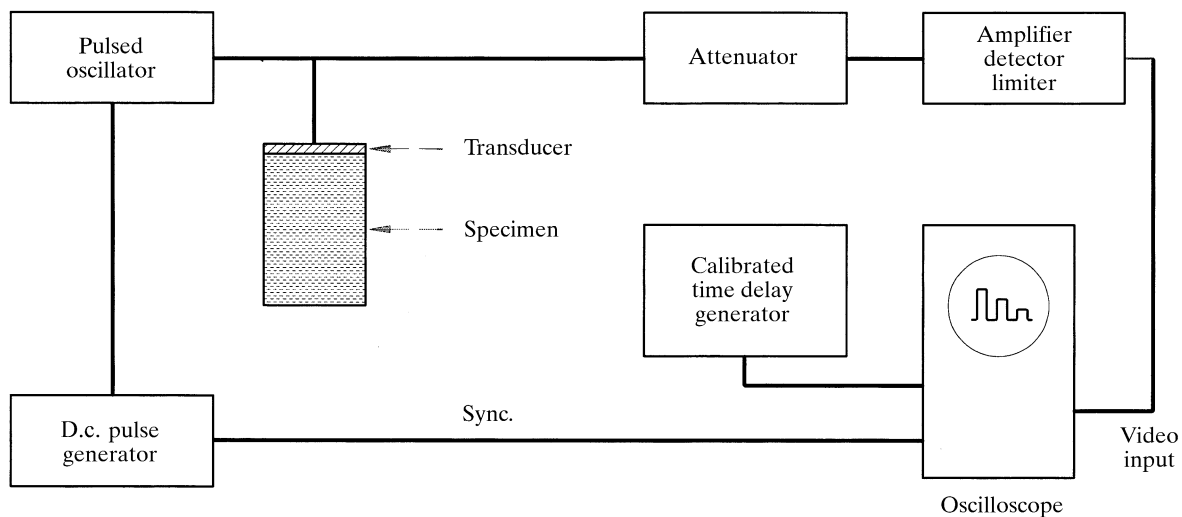


Fig. 1.3.4.2. Block diagram of the pulse-echo technique.