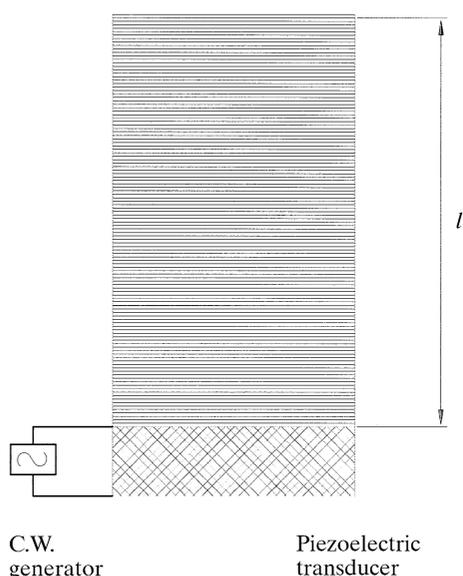## 1.3. ELASTIC PROPERTIES



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

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 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.

### 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 $\Theta_D$ is the Debye temperature, the elastic stiffnesses decrease according to a $\Theta^4$ law. From $\Theta_D/5$ to the beginning of the instability domain, the dependence is linear with $\Theta$. 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 stiffness is linear as long as the applied pressure is small compared to the elastic stiffnesses. As an example, a typical order of magnitude for $c_{11}$ in crystals is about 100 GPa and, within the experimental uncertainty, the pressure dependence of $c_{11}$ does not depart from a linear behaviour up to at least 0.2 GPa.

These observations can be quantitatively justified on the basis of an equation of state of a solid:
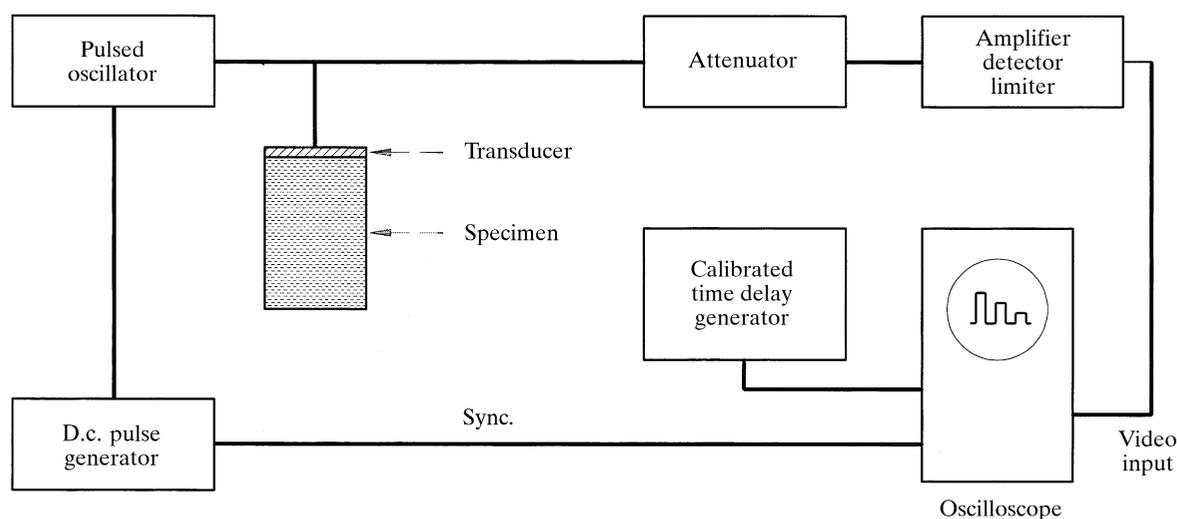
$$f(T_{ij}, S_{ij}, X, \Theta) = 0,$$



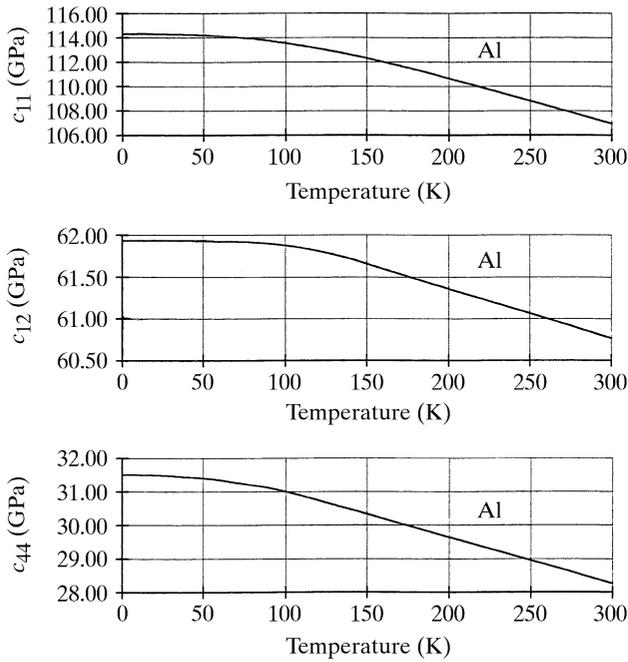Fig. 1.3.4.2. Block diagram of the pulse-echo technique.

Fig. 1.3.5.1. Temperature dependence of the elastic stiffnesses of an aluminium single crystal (after Every & McCurdy, 1992).

where $T_{ij}$ represents the stress tensor, $S_{ij}$ the strain tensor, $X$ the position of the elementary elements of the solid and $\Theta$ the temperature.

Different equations of state of solids have been proposed. They correspond to different degrees of approximation that can only be discussed and understood in a microscopic theory of lattice dynamics. The different steps in the development of lattice dynamics, the Einstein model, the Debye model and the Grüneisen model, will be presented in Section 2.1.2.7. Concerning the temperature and the pressure dependences of the elastic constants, we may notice that rather sophisticated models are needed to describe correctly the general trends mentioned above:

(a) In the *Einstein model*, where the $N$ atoms of a crystal are considered as $3N$ independent harmonic oscillators, the temperature increase affects only the amplitude of the oscillations and not the average positions of the atoms; consequently, this model can explain neither the thermal expansion nor the *temperature dependence* of the elastic constants. In addition, this theory ignores the difference between isothermal and adiabatic elastic constants. Similarly, if the oscillators are harmonic, the stiffness of the 'springs' connecting atoms does not depend on distances between atoms and the model cannot therefore explain the pressure dependence of the elastic constants, which requires anharmonic 'springs' or, more accurately, anharmonic potentials.

(b) In the *Debye model*, the $3N$ oscillators are not independent but they are still harmonic. The result is that here again the elastic constants are pressure and temperature independent.
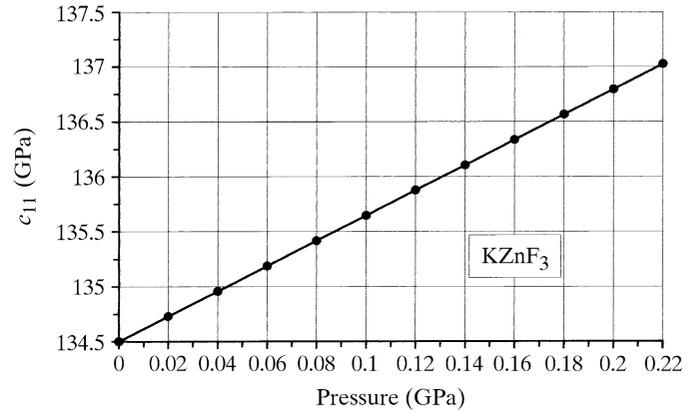


Fig. 1.3.5.2. Pressure dependence of the elastic stiffness $c_{11}$ of a KZnF$_3$ crystal. Reproduced with permission from *Ultrasonics Symposium Proc. IEEE* (Fischer *et al.*, 1980). Copyright (1980) IEEE.

(c) In the *Grüneisen model*, the frequencies of the oscillators are volume-dependent; this so-called 'quasiharmonic approximation' can justify the standard behaviour shown in Figs. 1.3.5.1 and 1.3.5.2.

### 1.3.5.2. *Temperature dependence of the elastic constants*

Table 1.3.5.1 gives typical values of $(\partial \ln c_{ij}/\partial \Theta)_p$ for some cubic crystals considered within their stability domain. In column 6, the 'elastic Debye temperature' of the crystal, $(\Theta_D)_{\mathrm{el}}$, has been calculated according to the formula

$$(\Theta_D)_{\mathrm{el}} = hv/k_B(3n/4\pi)^{1/3},$$

where $h$ is the Planck constant, $k_B$ is the Boltzmann constant, $v$ is an average velocity (see for instance De Launay, 1956) and $n$ is the number of atoms per unit volume.

It is interesting to compare $(\Theta_D)_{\mathrm{el}}$, the 'elastic Debye temperature', with $(\Theta_D)_{\mathrm{cal}}$, the 'calorimetric Debye temperature'. The definition of $(\Theta_D)_{\mathrm{cal}}$ will be given in Section 2.1.2.7. It results from the attempt at founding a universal description for the thermal properties of solids when the temperature is expressed as a reduced temperature, $\Theta/(\Theta_D)_{\mathrm{cal}}$; $(\Theta_D)_{\mathrm{cal}}$ is obtained from calorimetric measurements at low temperature. It is worth noting that accurate values of low-temperature elastic constants and low-temperature calorimetric measurements lead to an excellent agreement between $(\Theta_D)_{\mathrm{el}}$ and $(\Theta_D)_{\mathrm{cal}}$ [better than 2 or 3 K (De Launay, 1956)]. This agreement demonstrates the validity of the Debye model in the vicinity of 0 K. From Table 1.3.5.1, we can observe that for ionic crystals $(\partial \ln c_{11}/\partial \Theta)_p$ is, in general, greater than $(\partial \ln c_{44}/\partial \Theta)_p$. This remark is not valid for covalent and metallic crystals. Typical orders of magnitude are given in Table 1.3.5.2. These statements concern only general trends valid for stable crystals.

In the case of *temperature-induced phase transitions*, some elastic constants are softened in the vicinity and sometimes far from the critical temperature. As an example, Fig. 1.3.5.3 shows the temperature dependence of $c_{44}$ in RbCdF$_3$, CsCdF$_3$ and TlCdF$_3$ single crystals. RbCdF$_3$ and TlCdF$_3$ undergo structural phase transitions at 124 and 191 K, respectively, while CsCdF$_3$ remains stable in this temperature range. The softening of $c_{44}$ when the temperature decreases starts more than 100 K before the critical temperature, $\Theta_c$. In contrast, Fig. 1.3.5.4 shows the temperature dependence of $c_{11}$ in KNiF$_3$, a crystal that undergoes a para–antiferromagnetic phase transition at 246 K; the coupling between the elastic and the magnetic energy is weak, consequently $c_{11}$ decreases abruptly only a few degrees before the critical temperature. We can generalize this observation and state that the softening of an elastic constant occurs over a large domain of

Table 1.3.5.1. *Temperature dependence of the elastic stiffnesses for some cubic crystals*

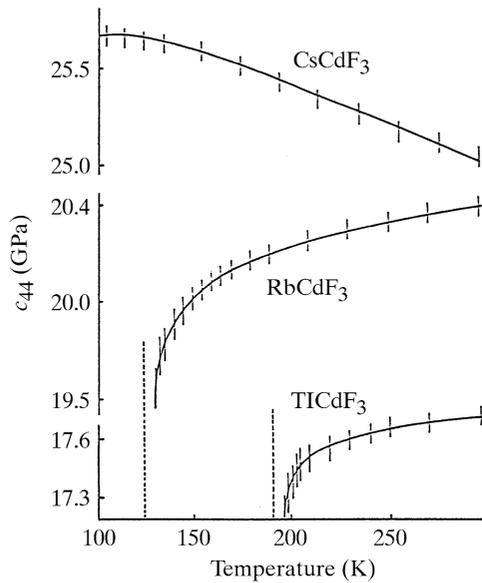| Material | Temperature range (K) | $(\partial \ln c_{11}/\partial \Theta)_p$ $(10^{-4}\,\mathrm{K}^{-1})$ | $(\partial \ln c_{44}/\partial \Theta)_p$ $(10^{-4}\,\mathrm{K}^{-1})$ | $(\partial \ln c_{12}/\partial \Theta)_p$ $(10^{-4}\,\mathrm{K}^{-1})$ | $\Theta^{\mathrm{el}}$ (K) |
|---|---|---|---|---|---|
| Al | 80–300 | −3.1 | −4.45 | −1.3 | 430 |
| Cu | 80–300 | −2.01 | −3.33 | −1.24 | 344 |
| Ag | 50–300 | −2.3 | −4.0 | −1.5 | 226 |
| Pb | 100–300 | −4.4 | −1.5 | −2.8 | 105 |
| Si | 80–300 | −0.81 | −10.6 | −1.10 | 648 |
| Ge | 150–1000 | −1.2 | −1.15 | −1.10 | 374 |
| ZnS | 100–300 | −1.2 | −0.65 | −0.8 | 347 |
| NaCl | 100–300 | −7.8 | −2.2 | −4.7 | 321 |
| KCl | 80–300 | −8.3 | −2.1 | −3.6 | 236 |
| KBr | 80–300 | −7.6 | −2.1 | 7 | 172 |

Fig. 1.3.5.3. Temperature dependence of the elastic constant $c_{44}$ in RbCdF$_3$, CsCdF$_3$ and TlCdF$_3$ crystals; the crystals of RbCdF$_3$ and TlCdF$_3$ undergo structural phase transitions (after Rousseau *et al.*, 1975).
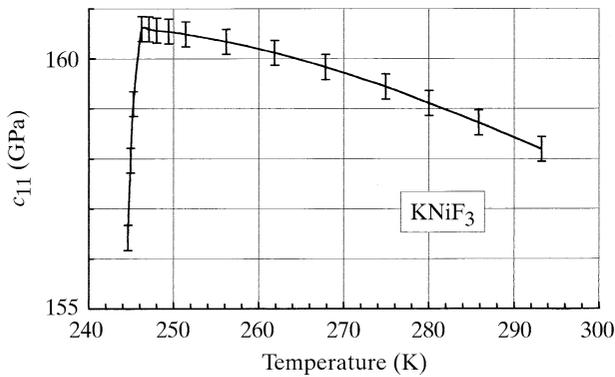


Fig. 1.3.5.4. Temperature dependence of the elastic constant $c_{11}$ in KNiF$_3$, which undergoes a para–antiferromagnetic phase transition. Reprinted with permission from *Appl. Phys. Lett.* (Nouet *et al.*, 1972). Copyright (1972) American Institute of Physics.

temperature when this constant is the order parameter or is strongly coupled to the order parameter of the transformation; for instance, in the cooperative Jahn–Teller phase transition in DyVO$_4$, $(c_{11} - c_{12})/2$ is the soft acoustic phonon mode leading to the phase transition and this parameter anticipates the phase transition 300 K before it occurs (Fig. 1.3.5.5).

### 1.3.5.3. *Pressure dependence of the elastic constants*

As mentioned above, anharmonic potentials are needed to explain the stress dependence of the elastic constants of a crystal. Thus, if the strain-energy density is developed in a polynomial in terms of the strain, only the first and the second elastic constants are used in linear elasticity (harmonic potentials), whereas higher-order elastic constants are also needed for nonlinear elasticity (anharmonic potentials).

Concerning the pressure dependence of the elastic constants (nonlinear elastic effect), considerable attention has been paid to

Table 1.3.5.2. *Order of magnitude of the temperature dependence of the elastic stiffnesses for different types of crystals*

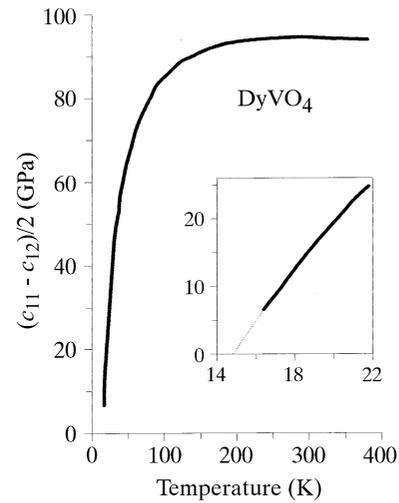| Type of crystal | $(\partial \ln c_{11}/\partial \Theta)_p$ (K$^{-1}$) | $(\partial \ln c_{44}/\partial \Theta)_p$ (K$^{-1}$) |
|---|---|---|
| Ionic | $-10^{-3}$ | $-3 \times 10^{-4}$ |
| Covalent | $-10^{-4}$ | $-8 \times 10^{-5}$ |
| Metallic | $-2 \times 10^{-4}$ | $-3 \times 10^{-4}$ |



Fig. 1.3.5.5. Temperature dependence of $(c_{11} - c_{12})/2$ in DyVO$_4$, which undergoes a cooperative Jahn–Teller phase transition (after Melcher & Scott, 1972).

their experimental determination since they are a unique source of significant information in many fields:

(i) In *geophysics*, a large part of the knowledge we have on the interior of the earth comes from the measurement of the transit time of elastic bursts propagating in the mantle and in the core (in the upper mantle, the average pressure is estimated to be about a few hundred GPa, a value which is comparable to that of the elastic stiffnesses of many materials).

(ii) In *solid-state physics*, the pressure dependence of the elastic constants gives significant indications concerning the stability of crystals. For example, Fig. 1.3.5.2 shows the pressure dependence of the elastic constants of KZnF$_3$, a cubic crystal belonging to the perovskite family. As mentioned previously, this crystal is known to be stable over a wide range of temperature and the elastic stiffnesses $c_{ij}$ depend linearly on pressure. It may be noted that, consequently, the third-order elastic constants (TOECs) are constant. On the contrary, we observe in Fig. 1.3.5.6 that the pressure dependence of the elastic constants of TlCdF$_3$, a cubic crystal belonging to the same family but which is known to become unstable when the temperature is decreased to 191 K (Fischer, 1982), is nonlinear even at low pressures. In this case, the development of the strain-energy density in terms of strains cannot be stopped after the terms containing the third-order elastic constants; the contributions of the fourth- and fifth-order elastic constants are not negligible.

(iii) For practical use in the case of technical materials such as concrete or worked metals, the pressure dependence of the elastic moduli is also required for examining the effect of applied stresses or of an applied hydrostatic pressure, and for studying residual stresses resulting from loading (heating) and unloading (cooling) the materials.
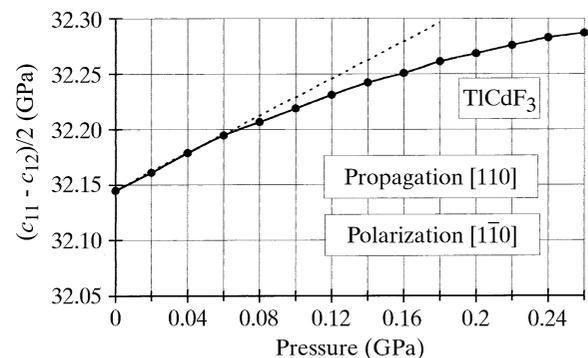


Fig. 1.3.5.6. Pressure dependence of the elastic constants $(c_{11} - c_{12})/2$ in TlCdF$_3$. Reproduced with permission from *Ultrasonics Symposium Proc. IEEE* (Fischer *et al.*, 1980). Copyright (1980) IEEE.

**references**