

1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

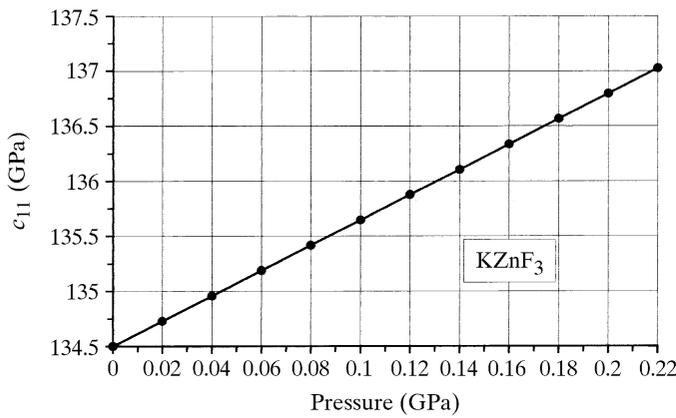


Fig. 1.3.5.2. Pressure dependence of the elastic stiffness c_{11} of a KZnF_3 crystal. Reproduced with permission from *Ultrasonics Symposium Proc. IEEE* (Fischer *et al.*, 1980). Copyright (1980) IEEE.

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:

$$f(T_{ij}, S_{ij}, X, \Theta) = 0,$$

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

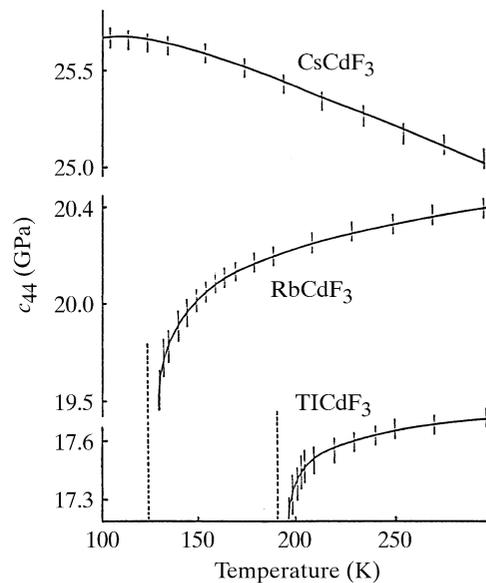


Fig. 1.3.5.3. Temperature dependence of the elastic constant c_{44} in RbCdF_3 , CsCdF_3 and TiCdF_3 crystals; the crystals of RbCdF_3 and TiCdF_3 undergo structural phase transitions (after Rousseau *et al.*, 1975).

(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, $(\Theta_D)_{el}$, has been calculated according to the formula

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

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 $(\Theta_D)_{el}$, the ‘elastic Debye temperature’, with $(\Theta_D)_{cal}$, the ‘calorimetric Debye temperature’. The definition of $(\Theta_D)_{cal}$ 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, $\Theta/(\Theta_D)_{cal}$; $(\Theta_D)_{cal}$ 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 $(\Theta_D)_{el}$ and $(\Theta_D)_{cal}$ [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 TiCdF_3 single crystals. RbCdF_3 and TiCdF_3 undergo structural phase transitions at 124 and 191 K, respectively, while CsCdF_3 remains stable in this temperature range.

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} K^{-1}) | $(\partial \ln c_{44} / \partial \Theta)_p$ (10^{-4} K^{-1}) | $(\partial \ln c_{12} / \partial \Theta)_p$ (10^{-4} K^{-1}) | Θ^{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 |