Anharmonic effects in crystals

If in the expression for the potential energy of interatomic interaction we limit ourselves to only quadratic terms in interatomic displacements (harmonic approximation), then

1. There would no thermal expansion.

2. Adiabatic and isothermal elastic constants would respectively be equal to each other.

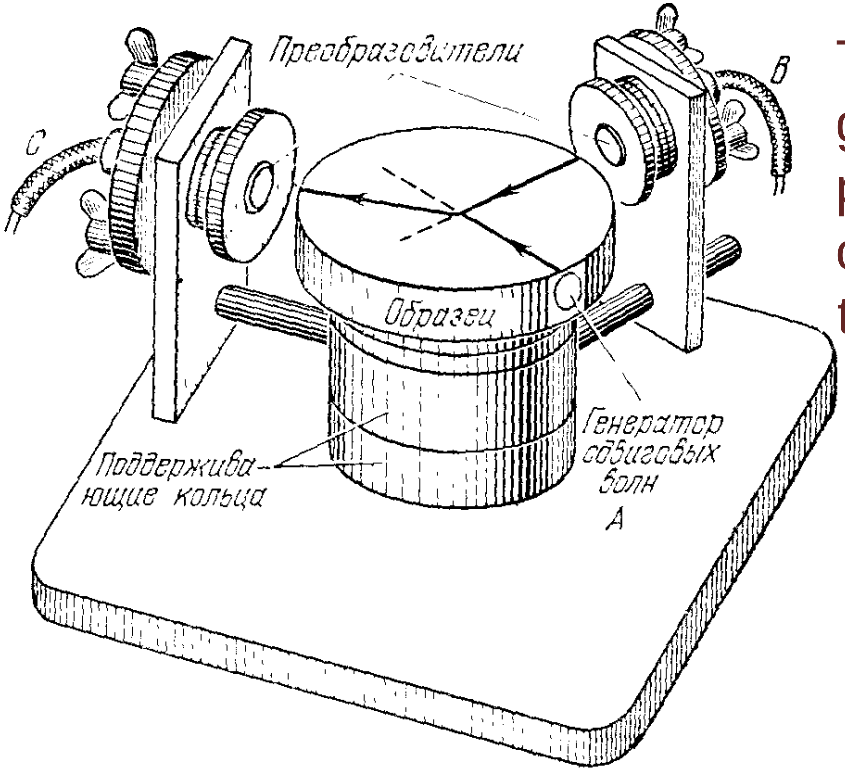
3. Elastic constants would not depend on pressure and temperature.

4. Heat capacity at high temperatures ($T > \theta$) would be constant.

5. Two elastic waves in a lattice do not interact with each other, a separate wave does not decay or change its shape over time, and phonons do not scatter on each other.

All this is not true in real crystals with anharmonic terms in the interatomic interaction .

Demonstration of three-phonon interactions



The amplitude of the generated beam is proportional to the product of the amplitudes of the two source beams:

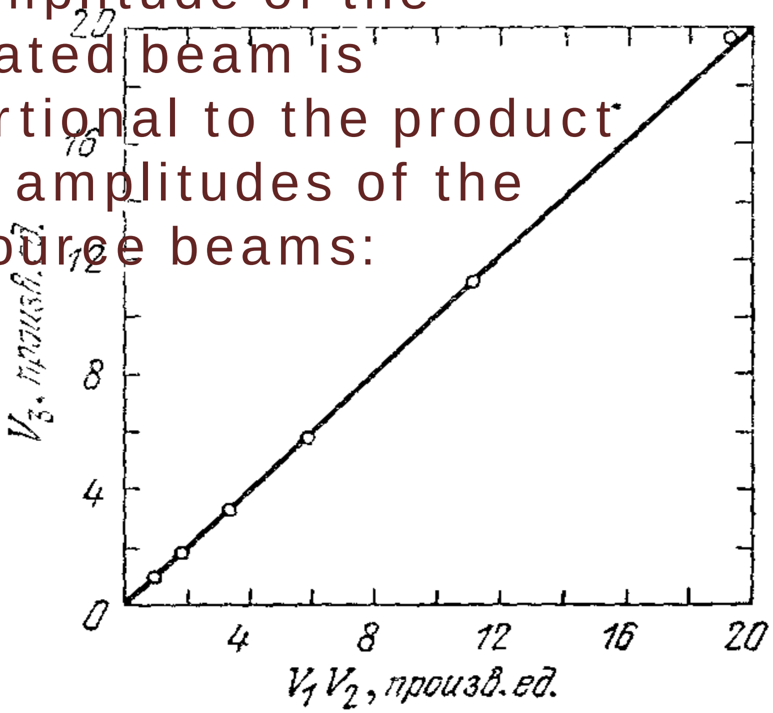


Diagram of the ultrasonic setup used to conduct the experiment demonstrating three-phonon interaction. In a typical experiment, generator A excited shear waves with a frequency of 10 MHz, which interacted near the center of the sample (which had the shape of a disk) with longitudinal waves with a frequency of 15 MHz, which were excited by generator B. The longitudinal wave with a frequency of 25 MHz resulting from the interaction was recorded by receiver C, and the relationship for wave vectors: K1 + K1 = K3 was satisfied.

Thermal expansion.

Three-phonon processes are caused by cubic terms in potential energy, for example

$$U_{\text{куб}} = A e_{xx} e_{yy} e_{zz}$$

They are also responsible for thermal crystal expansion:

$$U(x) = cx^2 - gx^3 - fx^4,$$

We calculate the average displacement value from the Boltzmann distribution:

$$\langle x \rangle = \left(\int_{-\infty}^{\infty} dx\, x e^{-U(x)/\tau} \right) \left(\int_{-\infty}^{\infty} dx\, e^{-U(x)/\tau} \right)^{-1}$$

$$\int dx\, x e^{-U(x)/\tau} \approx \int dx\, e^{-cx^2/\tau} \left(x + \underline{\frac{1}{\tau} g x^4} + \frac{1}{\tau} f x^5 \right) = \frac{3\pi^{1/2}}{4} \frac{g}{c^{5/2}} \tau^{3/2}$$

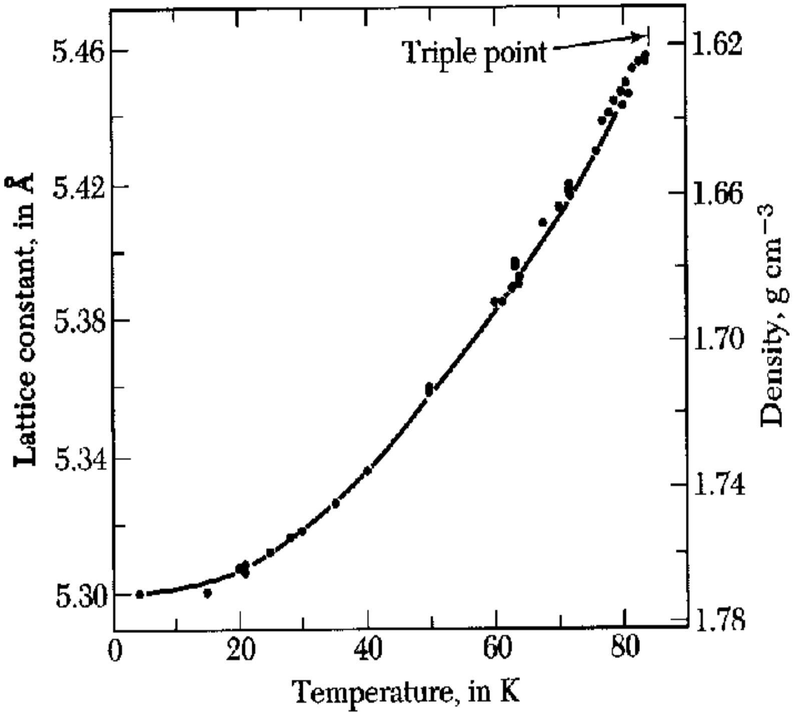
$$\int dx\, e^{-U(x)/\tau} \approx \int dx\, e^{-cx^2/\tau} = \left(\frac{\pi\tau}{c} \right)^{1/2}$$

Only even powers of x give nonzero contribution

In the classical case for <x> we get:

$$\langle x \rangle = \frac{3g}{4c^2} k_B T.$$

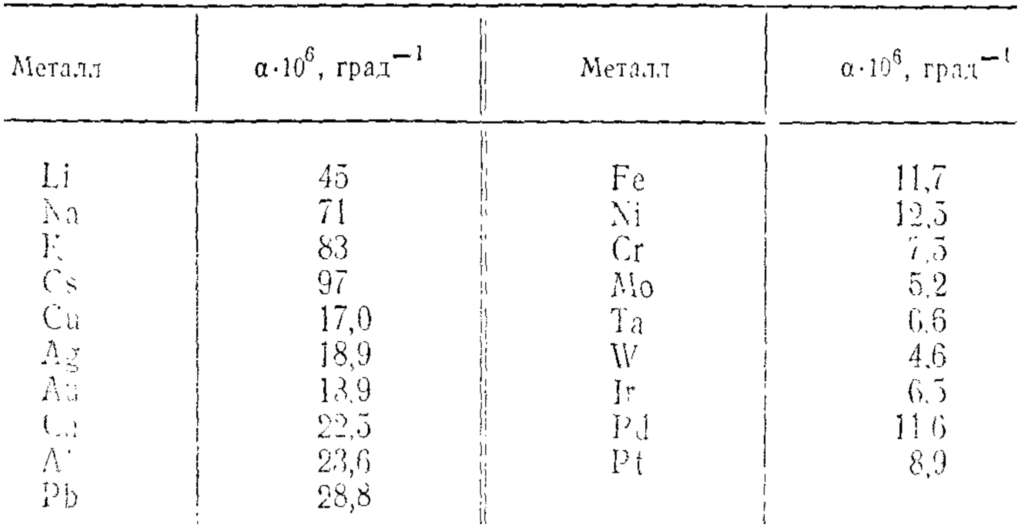
Experimental data on the coefficient of thermal expansion



Interatomic distance in the lattice of solid argon as a function of temperature

Coefficients of linear thermal expansion near room temperature

$$\alpha = \frac{1}{l}\frac{\partial l}{\partial T}$$



Металл	$\alpha\cdot10^6$, град$^{-1}$	Металл	$\alpha\cdot10^6$, град$^{-1}$
Li	45	Fe	11,7
Na	71	Ni	12,5
K	83	Cr	7,5
Cs	97	Mo	5,2
Cu	17,0	Ta	6,6
Ag	18,9	W	4,6
Au	13,9	Ir	6,5
Ca	22,5	Pd	11,6
Al	23,6	Pt	8,9
Pb	28,8		

In harmonic approximation the energy of an atom is assumed to be

$$E_i = E_i^0 + a\left(\vec{r} - \vec{r}_0\right)^2 , \qquad (6.1)$$

where the second term on the right-hand side is the energy of oscillations. In this approximation phonons are independent from one another. In other words, there is no phonon-phonon scattering.

Inclusion the third-order term in the energy expansion

$$E_i = E_i^0 + a\left(\vec{r} - \vec{r}_0\right)^2 + b\left(\vec{r} - \vec{r}_0\right)^3 \qquad (6.2)$$

accounts the phonon-phonon interaction.

Thermal expansion and the Grüneisen parameter

Equation (6.2) leads to non-zero thermal expansion; in harmonic approximation the thermal expansion is zero.

We can, however, partly account for anharmonic forces, if in harmonic approximation (6.1) assume that the force constant a depends on the volume.

This approximation is known as quasielastic.

If the lattice force constants depend on the volume, the frequencies of the normal modes also depend on the volume.

From thermodynamic considerations, the equation of state of a crystal can be written as

$$p = -\frac{\partial}{\partial V}\left(U_{\text{eq}} + \sum_i \tfrac{1}{2}\hbar\omega_i \right) + \sum_i \left(-\frac{\partial}{\partial V}\left(\hbar\omega_i\right)\right) \frac{1}{e^{\hbar\omega_i/k_B T} - 1}. \qquad (6.3)$$

The thermal expansion coefficient is

$$\alpha = \frac{1}{l}\left(\frac{\partial l}{\partial T}\right)_p = \frac{1}{3V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{3B}\left(\frac{\partial p}{\partial T}\right)_V , \qquad (6.4)$$

where

$$B = -V\left(\frac{\partial p}{\partial V}\right)_T$$

is the bulk modulus.

Substituting (6.3) in (6.4) we find

$$\alpha = \frac{1}{3B}\sum_i \left(-\frac{\partial}{\partial V}\hbar\omega_i \right)\frac{\partial}{\partial T} n_i \ , \tag{6.5}$$

where

$$n_i = \frac{1}{e^{\hbar\omega_i/k_B T} - 1} \ .$$

The contribution of each vibrational mode to the specific heat is

$$C_i = \frac{\hbar\omega_i}{V}\frac{\partial}{\partial T} n_i \ . \tag{6.6}$$

For each vibrational mode i we can introduce the quantity

$$\gamma_i = -\frac{V}{\omega_i}\frac{\partial \omega_i}{\partial V} = -\frac{\partial \ln \omega_i}{\partial \ln V} \ , \tag{6.7}$$

known as the **Grüneisen parameter**.

We now determine the average Grüneisen parameter

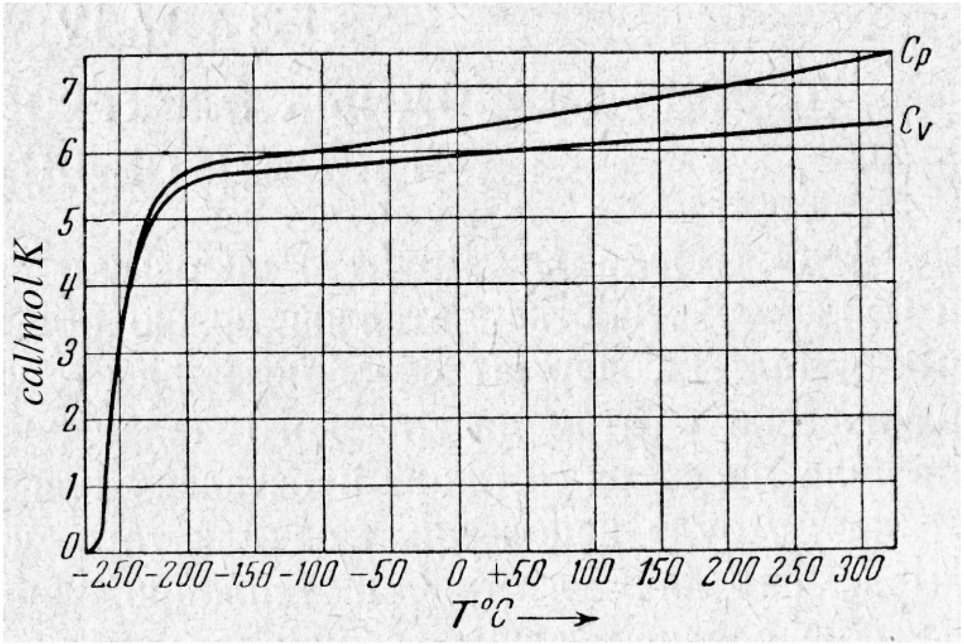
$$\gamma = \left(\sum_i \gamma_i C_i\right) \Big/ \left(\sum_i C_i\right) \tag{6.8}$$

and find that

$$\alpha = \frac{\gamma C_V}{3B} \ . \tag{6.9}$$

Since the bulk modulus is only weakly temperature dependent, the models assuming the constant Grüneisen parameter predict for the thermal expansion coefficient the same temperature variation as for the specific heat.

Finally, we note that the approximately linear-in-temperature increase of C_V at high temperatures is also a consequence of lattice anharmonicity.



[from F. Seitz, *Modern Theory of Solids*, (McGraw-Hill, New York, 1940)]