Appendix 15
Thermal Properties of Layered Crystals

Debye's theory provides a reasonable interpolation between the thermal properties of crystals at the high and the low temperature for crystals of relatively simple structure. In the case of strong anisotropy (layered crystals) a new range of temperatures appears in which a new universal theory (*I.M. Lifshits, 1952*) is valid.

Vibrations

In layered crystals, the coupling between the layers is weaker that that within the layer. If the wave vector $\mathbf{k}$ is split into its component $\mathbf{q}$ parallel to the layer and that k perpendicular to it, then three acoustic modes with polarisations parallel to the layer (longitudinal and transverse) and perpendicular to it have the frequencies

$$\omega_l^2 = U_l^2 q^2 + u^2 k^2; \quad \omega_t^2 = U_t^2 q^2 + u^2 k^2; \quad \omega_z^2 = u^2 q^2 + u_{12}^2 k^2 + \gamma^2 q^4, \tag{1}$$

where U_l, U_t and γ are properties of an isolated layer, while u and u_{12} characterise the weak coupling between the layers. $(u/U = \eta,\, \eta \ll 1)$. The Debye temperature Θ has usual order magnitude $\Theta \sim \hbar U/a$, where a is inter-atomic distance, while the dispersion of $\omega_{l,t}$ as a function of k is only $\Delta\omega_{l,t} \sim \eta^2 \Theta/\hbar$. The bending mode ω_z is dominated in small wave vectors $\mathbf{q}$ by the the bending rigidity γ of isolated layer. This rigidity γ appears beyond the elasticity theory if dispersion of $\omega_z(q)$ is taken into account. It will be assumed that this rigidity has usual atomic order of magnitude $\gamma \sim Ua$. Dispersion law $\omega(q)$ for all three acoustic modes is shown in Fig 1. It shows that the softest of three acoustic modes always is the bending mode with the frequency ω_z.

Specific Heat

Specific heat C of a layered crystal has four ranges of temperature T. At $T \gg \Theta$, the classical statistics is valid and specific heat is a constant.

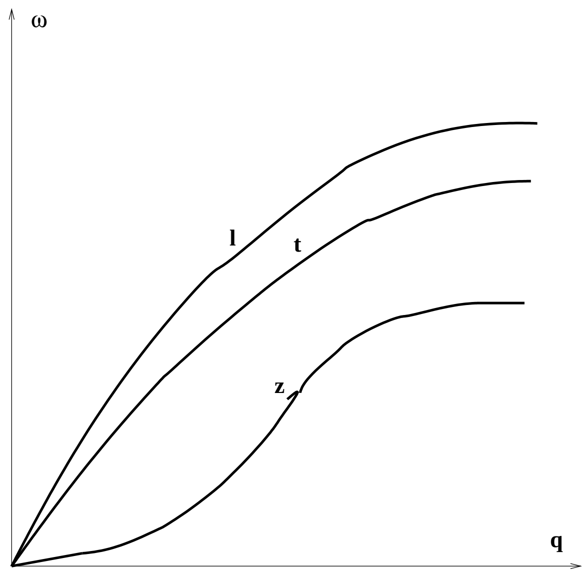

Figure 1: Dispersion of acoustic modes in a layered crystal

At $\eta\Theta \ll T \ll \Theta$ the contribution of the bending mode dominates the thermodynamics, but all inter-layer coupling constants u and u_{12} could be neglected as well as whole k-dispersion. Therefore

$$F - F_0 \propto T \int (d\mathbf{q}) \ln \left\{ 1 - \exp\left(-\frac{\hbar\gamma q^2}{T} \right) \right\} \propto T^2, \quad C \propto \frac{T}{\Theta}. \tag{2}$$

At $\eta^2\Theta \ll T \ll \eta\Theta$, the contribution of the bending mode still dominates the thermodynamics but its k-dispersion should be taken into account:

$$F - F_0 \propto T \int dk (d\mathbf{q}) \ln \left\{ 1 - \exp\left(-\frac{\hbar\sqrt{\gamma^2 q^4 + u_{12}^2 k^2}}{T} \right) \right\} \propto T^3, \quad C \propto \frac{T^2}{\eta\Theta^2}. \tag{3}$$

Finally, at $T \ll \eta^2\Theta$, the Debye law T^3 re-appears

$$C \propto \frac{T^3}{\eta^3\Theta^3}, \tag{4}$$

with the enhancing factor η^{-3}.

Thermal expansion

Thermal expansion is determined by the tensor $\hat{\alpha}$:

$$\alpha_{ij} = \frac{\partial u_{ij}}{\partial T} = 3\,\frac{\partial^2 \Phi}{\partial \sigma_{ij} \partial T}\ ,$$

where $\Phi(\hat{\sigma}, T)$ is the Gibbs free energy at given stress $\hat{\sigma}$. In the layered crystals, thermal expansion is anisotropic. If the crystal has tetrahedral or higher symmetry, thermal expansion there are two independent components α_{zz} and $\alpha_{||} = \alpha_{xx} = \alpha_{yy}$). Assume that the sample is the subject the pressure p_z perpendicular to the plane of the layers and the pressure p in the plane. The stress tensor is

$$\hat{\sigma} = -\frac{1}{3}\begin{pmatrix} p & 0 & 0 \\ 0 & p & 0 \\ 0 & 0 & p_z \end{pmatrix}\ ,$$

and coefficients of thermal expansions are

$$\alpha_{xx} = -\frac{\partial^2 \Phi}{\partial p \partial T}, \qquad \alpha_{zz} = -\frac{\partial^2 \Phi}{\partial p_z \partial T}.$$

Since

$$\Phi = \Phi_0 + T \sum_s \int (d\mathbf{k}) \ln\left(1 - \exp\left[-\frac{\hbar\omega(\mathbf{k})}{T}\right]\right)\ , \tag{5}$$

thermal parts of strain tensors $\hat{u}$ are

$$u_{zz} = -\hbar\ \sum_s\ \int (d\mathbf{k})\ n_B\left(\frac{\hbar\omega_s(\mathbf{k})}{T}\right)\ \frac{\partial \omega_s(\mathbf{k})}{\partial p_z} \tag{6}$$

$$u_{xx} = -\hbar\ \sum_s\ \int (d\mathbf{k})\ n_B\left(\frac{\hbar\omega_s(\mathbf{k})}{T}\right)\ \frac{\partial \omega_s(\mathbf{k})}{\partial p} \tag{7}$$

When an external pressure is applied, the frequency of the bending mode ω_z is given by the following expression

$$\omega_z^2(\mathbf{q}) = \frac{p}{\rho}\ \mathbf{q}^2 + \gamma\mathbf{q}^4 \tag{8}$$

It is clear from Eq (8) that $\partial\omega(\mathbf{q})/\partial p$ is not small even in quadratic in $\mathbf{q}$ approximation and, therefore, the quartic term in Eq (8) could be neglected when this derivative is calculated. Since $\partial\omega(\mathbf{q})/\partial p > 0$, the contribution of the bending mode into $\alpha_+ xx$ is negative (*thermal contraction*). Therefore, it follows from Eq (8) that

$$\frac{\partial \omega_z(\mathbf{q})}{\partial p} = \frac{\mathbf{q}^2 + uk^2}{2\rho c\sqrt{\eta^2\mathbf{q}^2 + \zeta^2 k^2 + (a^2\nu^2/\pi^2)\mathbf{q}^4}} \tag{9}$$

At $T \ll \eta^2\Theta$ the usual law $\alpha \propto T^3$ is valid.
At $\eta^2\Theta \ll T \ll \eta\Theta$ the thermal expansion follows the law:

$$\alpha_{xx} \propto -T, \quad \alpha_{zz} \propto T^2 \tag{10}$$

Fluctuations and Mössbauer Effect

Fluctuations of the displacements $\mathbf{u}$ of the atoms in a layered crystal are very different, depending of direction of this displacement, because the displacements parallel to the plane of the layer are determined by the rigid longitudinal and transverse modes, while the displacements perpendicular to the plane are determined by the soft bending mode. Therefore,

$$\langle u_z^2 \rangle = \int \frac{dk}{2\pi} \int \frac{\hbar \ (d\mathbf{q})}{4m \ \omega_z(k, \mathbf{q})} \coth \frac{\omega_z(k, \mathbf{q})}{2T} \tag{11}$$

At absolute zero

$$\langle u_z^2 \rangle_0 = \int \frac{dk}{2\pi} \int \frac{\hbar \ (d\mathbf{q})}{4m \ \omega_z(k, \mathbf{q})} \propto \frac{1}{a} \int \frac{(d\mathbf{q})}{\omega_z(a^{-1}, \mathbf{q})} \propto \langle u^2 \rangle_0 \ \ln \frac{1}{\eta}, \tag{12}$$

where $\langle u^2 \rangle_0$ is the range of fluctuation in the parallel direction within an isolated layer. Thermal fluctuations differ for different temperature ranges. For $T \gg \eta\Theta$

$$\langle u_z^2 \rangle_T \propto T \ \int \frac{dk}{2\pi} \int \frac{(d\mathbf{q})}{\omega_z^2(k, \mathbf{q})} \propto \langle u^2 \rangle_0 \cdot \frac{T}{\eta \ \Theta}, \quad T \gg \eta\Theta. \tag{13}$$

For $\eta^2\Theta \ll T \ll \eta\Theta$

$$\langle u_z^2 \rangle_T \propto \int \frac{dk}{2\pi} \int \frac{(d\mathbf{q})}{\omega_z(k, \mathbf{q})} n_B \left(\frac{\omega_z^2(k, \mathbf{q})}{T} \right) \propto \langle u^2 \rangle_0 \cdot \frac{T}{\eta \ \Theta} \ln \frac{\eta\Theta}{T}, \quad \eta\Theta \ll T \ll \Theta. \tag{14}$$

Here the Bose distribution functions $n_B(x)$ is

$$n_B(x) = \frac{\coth(x/2) - 1}{2} = \frac{1}{e^x - 1}.$$

And for $T \ll \eta^2\Theta$,

$$\langle u_z^2 \rangle_T \propto \langle u^2 \rangle_0 \cdot \left(\frac{T}{\eta \ \Theta} \right)^3, \quad T \ll \eta^2\Theta. \tag{15}$$

In all cases, the fluctuations in the perpendicular direction is parametrically larger, than those in the parallel one.

Coming to the physical problem of calculation the reduction factor $\exp[-w]$ of the recoilless γ-ray emission by the nucleus in the layered crystal (the Mössbauer effect), we could see that the factor w differs strongly depending on direction of γ-rays emission. If γ-rays are emitted in direction perpendicular to the plane of the layers, the factor w is parametrically larger than that for direction of emission parallel to the plane of the layers. Calculated mean square of fluctuations $\langle u_z^2 \rangle$, gives an estimate of the factor w.

Spin-lattice relaxation

Spin-lattice relaxation at low temperature is determined by rate of nearly elastic spin-flip scattering of the phonons on local spins. In ordinary crystals, the rate of relaxation τ_1^{-1} is

$$\frac{1}{\tau_1} \propto \begin{cases} (T/\Theta)^2, & T \gg \Theta \\ (T/\Theta)^7, & T \ll \Theta \end{cases}$$

Returning to the layered crystals and assuming that the dominant contribution comes from the bending mode we arrive at the following estimate for the rate of relaxation:

$$\frac{1}{\tau_1} \propto \int \frac{dk}{2\pi} \int (d\mathbf{q}) \frac{k^4}{\sinh^2\left[\omega_z/2T\right]} \tag{16}$$

At $T \gg \eta\Theta$

$$\frac{1}{\tau_1} \propto \left(\frac{T}{\eta\Theta}\right)^2 \quad T \gg \eta\Theta. \tag{17}$$

At $\eta^2\Theta T \ll \eta\Theta$

$$\frac{1}{\tau_1} \propto \eta \left(\frac{T}{\eta\Theta}\right)^6 \quad \eta^2\Theta \ll T \ll \eta\Theta. \tag{18}$$

And at $T \ll \eta^2\Theta$

$$\frac{1}{\tau_1} \propto \left(\frac{T}{\eta\Theta}\right)^7 \quad T \ll \eta^2\Theta. \tag{19}$$

A simple check out verifies the assumption that the rate of spin lattice relaxation is dominated by the contribution of the bending mode.