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ENTROPY OF THE (00.1) FACE OF GRAPHITE

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The phonon surface entropy of many cubic crystals has been recently calculated by Dobrzynski and Friedel[1]). The agreement with a few experimental evaluations is satisfactory.

The purpose of this note is to compute the surface phonon entropy of an hexagonal crystal here, graphite, and compare the result with an indirect experimental determination.

Theoretical determination

In the high temperature limit the vibrational surface entropy for the unit cell is given by[1]):

$$\Delta S = \frac{k}{2}\left[\mathrm{Tr}\ln\lambda - \mathrm{Tr}\ln\lambda' + \sum_m \frac{(-1)^m}{m}\left[\mathrm{Tr}(\lambda'^{-1}R')^m - \mathrm{Tr}(\lambda^{-1}R)^m\right]\right]$$

where k is the Boltzmann constant, λ is the diagonal part of the dynamical matrix D of the bulk, and R is the remainder; λ' and R' are the similar matrix for the dynamical matrix D' of the surface obtained by cutting the atomic interaction on one side; $[\mathrm{Tr}(\lambda'^{-1}R')^m - \mathrm{Tr}(\lambda^{-1}R)^m]$ is the average difference between the traces of the matrices $(\lambda'^{-1}R')^m$ and $(\lambda^{-1}R)^m$ for the wave vectors in the first Brillouin zone. The dynamical matrices D and D' of graphite were previously determined[2,3]) using the harmonic approximation and a simple lattice dynamic model. The assumptions for this model are as follows:

(a) non-central forces;

(b) first neighbor interaction inside and outside of the layer;

(c) crystal in the shape of parallelepiped including $N \cdot n \cdot n$ cells, N denoting the number of cells normal to the (00.1) face, and n the number of cells in the two other directions;

(d) free vibrations in both (00.1) and (00.$\bar{1}$) faces, satisfying the cyclic conditions of Born for the four other faces.

Introducing D and D', i.e. λ, λ', R, R' in ref. 4 we obtain the surface phonon entropy. Summation has been made with m ranging from 1 to 60. Computation of the average over the first Brillouin zone shows that the result is independent of the number of wave vectors.

We obtained:

$$\mathrm{Tr}\ln\lambda - \mathrm{Tr}\ln\lambda' = 0.046\,.$$

While:

$$\sum_{m=1}^{60} \frac{(-1)^m}{m}\left[\mathrm{Tr}\,(\lambda'^{-1}R')^m - \mathrm{Tr}\,(\lambda^{-1}R)^m\right] = 0.261\,,$$

then

$$\Delta S = 0.041\ \mathrm{erg\,cm^{-2}\,^\circ K^{-1}}$$

In our model the contribution of the summation is important, whereas Dobrzynski and Friedel[1]) demonstrate the opposite for cubic crystals. This means that the Einstein model fits fairly well the surface entropy of cubic crystals but not the surface entropy of graphite. This result is due to the introduction of important non-central forces in our model[2]), whereas the cubic crystals of Dobrzynski and Friedel have only central forces.

One can notice the low value of ΔS for the (00.1) face, which can be explained by the very strong bonds in this plane, and the very weak interactions between layers.

Experimental determination

Surface entropy of graphite was deduced from the experimental measurement of surface and bulk Debye temperatures. Let us suppose that:

$$S = \tfrac{1}{3}S_\perp + \tfrac{2}{3}S_\parallel \quad \text{and} \quad S' = \tfrac{1}{3}S'_\perp + \tfrac{2}{3}S'_\parallel\,.$$

Here S is the entropy of an infinite crystal and S' is the entropy of a crystal with a (00.1) surface; $\frac{1}{3}S_\perp$, $\frac{1}{3}S'_\perp$, $\frac{1}{3}S_\parallel$ and $\frac{1}{3}S'_\parallel$ are the contributions to the entropy of the vibrations in directions respectively perpendicular and parallel to plane (00.1) in the infinite and finite crystal.

It was shown[3]) that the mean square displacement of the atoms in the plane are the same for the bulk and the surface of graphite; then:

$$S_\parallel = S'_\parallel\,.$$

Hence the surface entropy ΔS is:

$$\Delta S = S' - S = \tfrac{1}{3}(S'_\perp - S_\perp)\,.$$

$S_\perp$ was calculated with a Debye model[4]) where entropy is a tabulated function of bulk Debye temperature. Its experimental value[3]) is 800 °K; S' was also calculated by the same method, but with a surface Debye temperature of 690 °K measured experimentally[3]).

We obtain for a temperature of 2000 °K:

$$\Delta S = 0.08\ \mathrm{erg\,cm^{-2}\,^\circ K^{-1}}\,.$$

This determination is nearly constant if the temperature is higher than $\Theta_{\perp B}$ and is of the same order of magnitude as the theoretical computation of surface entropy. The agreement is as good as the one obtained by Dobrzynski et al.'s[1]) calculation for cubic crystals. The product of surface entropy and temperature may be compared to the surface specific energy of graphite calculated by Crowell[5]) (~ 170 erg/cm^2). Whereas the contribution of entropy to the free surface specific energy is generally low, it cannot be neglected at high temperature for graphite. For instance our theoretical evaluation shows that $T\Delta S \sim 40$ erg/cm^2 at 1000°K.

The differences between our experimental and theoretical values may originate from the roughness and the imprecision of the models, and the scatter in the experimental data.

As a conclusion, the theoretical determination of surface phonon entropy is not very far from an indirect experimental evaluation. In contrast to cubic crystals for which the Einstein model provides with fair results, such an approximation is not valid in the calculation of the surface entropy of graphite. Finally the contribution of entropy to the specific free energy of surface is not negligible.

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