

**On defects in solids**

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**Abstract**

The thermodynamical potential for dilute solutions is rederived, generalized and applied to defects in solids. It is shown that there are always defects in solids, *i.e.* there is no perfect solid at any finite temperature. Apart from the temperature-dependent concentration of defects, another case is presented, where the defect concentration does not depend on temperature.

With standard notations we may write

$$dE = -pdV + TdS + \mu dN \quad (1)$$

at equilibrium, whence

$$d(E + pV - TS - \mu N) = Vdp - SdT - Nd\mu \quad (2)$$

We may introduce the thermodynamical potential

$$\Theta = E + pV - TS - \mu N \quad (3)$$

and, noticing that  $E$ ,  $V$ ,  $S$ ,  $N$  are extensive, while  $p$ ,  $T$  and  $\mu$  are intensive quantities, we have  $\Theta = \partial\Theta/\partial N \cdot N$ . On the other hand, we have from (2)  $\partial\Theta/\partial N = 0$  at equilibrium, whence  $\Theta = 0$ ; which corresponds to the definitions  $\Phi = E + pV - TS = \mu N$  of the thermodynamical potential  $\Phi$ .

Suppose that in a solid of  $N_0$  sites we are interested in the existence of  $n$  defects at fixed  $p, T$  and  $\mu$ , where  $n \ll N_0$ , but both  $n$  and  $N_0$  are very large. These defects are supposed to be structureless, and may be exemplified by vacancies, broken bonds, substitutional impurities, etc. (In other cases, as for interstitial atoms for instance, we may use the potential  $\Phi$ , corresponding to fixed  $N$ , with the same results as those to be derived below.) For each of them we have a variation  $\varepsilon$  of the energy, a variation  $v$  of the volume and a heat  $q$ , such that

$$\varepsilon = -pv + q + \mu \quad (4)$$

For instance, when a vacancy is created, for which  $v$  and  $\mu$  appear in (4) with the minus sign, the solid receives the heat  $q$  and the mechanical work  $-pv$  (the latter by the relaxation of the atomic surrounding), increases its energy by  $\varepsilon$  and loses an amount of energy equal to the chemical potential  $\mu$ . On the other hand, there is an increase in entropy

$$S = \ln C_{N_0}^n \quad (5)$$

where  $C_{N_0}^n = N_0!/n!(N_0 - n)!$ , due to the disorder created by the  $n$  ( $\ll N_0$ ) defects. For  $n$  and  $N_0$  large enough and  $n \ll N_0$  we may also write

$$C_{N_0}^n = \frac{N_0!}{n!(N_0-n)!} = \frac{N_0^{N_0}}{n^n(N_0-n)^{N_0-n}} = \left(\frac{N_0}{n}\right)^n \cdot \frac{(1-n/N_0)^n}{(1-n/N_0)^{N_0}} \approx \approx \left(\frac{N_0 e}{n}\right)^n, \tag{6}$$

whence

$$S \approx n \ln \left(\frac{N_0 e}{n}\right). \tag{7}$$

The thermodynamical potential  $\Theta$  given by (3) may therefore be expressed as

$$\Theta = \Theta_0 + (\varepsilon + pv - \mu)n + Tn \ln \left(\frac{n}{N_0 e}\right), \tag{8}$$

where  $\Theta_0$  is the value of  $\Theta$  at  $n = 0$  (homogeneous phase); or, using (4), we have

$$\Theta = \Theta_0 + qn + Tn \ln \left(\frac{n}{N_0 e}\right). \tag{9}$$

This is the generalization for the potential  $\Theta$  of the well-known expression[1] of the thermodynamical potential  $\Phi$  (*i.e.* at fixed  $N$ ) for dilute solutions.

At equilibrium we should have  $\Theta = 0$  and  $\partial\Theta/\partial n = 0$ . Here we distinguish two cases, but first we remark that the heat  $q$  should always be positive; otherwise the solid would be unstable. Then, we remark that an entropy  $s$  is created by producing a defect, accounted by the degree of local disorder generated on this occasion (which amounts to saying that actually the defects have a structure). If the process of creating the defects is a non-equilibrium process, *i.e.* if the defects are created fast enough in comparison with the relaxation time of the solid, then  $q < sT$  and, from the equilibrium condition, we have

$$n = N_0 e^{-q/T} \tag{10}$$

and  $\Theta_0 = Tn$ ; which means that we always have defects in solid (for any  $T \neq 0$ ), whose concentration increases with increasing the temperature, as it is well-known. In the second case, the defects may be created by an equilibrium process, *i.e.* by a process that is slow enough in comparison with the relaxation time of the solid, so that  $q = sT$ . From the equilibrium conditions we get in this case

$$n = N_0 e^{-s}, \tag{11}$$

*i.e.* there always exists (for any  $T \neq 0$ ) a finite concentration of defects, which is independent of temperature. In general, for any realistic values of  $q$  and  $s$ , and normal temperatures, the defect concentration given by both (10) and (11) is extremely low.

The first case, given by (10), of defect concentration increasing with temperature, represents a rather common situation, which is well documented. The second case, of a constant defect concentration as given by (11), has been brought into discussion more recently. For example, a constant, temperature independent concentration of vacancies has been invoked [2][3] in some alkali doped fullerides, in order to explain a certain feature in the *NMR* spectrum of the alkali nuclei, called the  $T - T'$  splitting.

Perhaps it is also appropriate to discuss here another aspect of this problem, concerning the relevance the defects may bear on the existence of the low-dimensional solids. The results presented here show that defects are always present in solids at any non-vanishing temperature. For a one-dimensional solid this means that the solid may be fragmented into pieces, of a certain average length, as given by (10) or (11). However, it may happen, as for instance in the first case (10) at low enough temperatures, that this average length be still large enough for the fragments have a thermodynamical behaviour. In this case it is known that a one-dimensional solid, irrespective of temperature, does not exist, in the sense that it is unstable with respect to the propagation of the long-wavelength phonons. A similar situation appears for a two-dimensional solid at  $T \neq 0$ , though here the defects are irrelevant (as well as in three dimensions) for the propagation of the long-wavelength phonons. It has been shown that the realistic experimental conditions always require a certain constraint upon the low-dimensional solids, which render them stable under the propagation of the long-wavelength phonons, so that the question of the melting of these solids is meaningful. All these questions are discussed in Ref.4,5, where the melting temperature has been estimated by means of a mean-field theory as being that temperature beyond which the solid gets soft and is no longer able to bear phonons. Very likely this melting temperature is an overestimation, and the melting defined in this way is intertwined with a continuous transition toward a state with a variable range of crystallinity in one dimension (as indicated by (10) for example), and with a subsequent state with extended, topological defects in two dimensions.

## References

- [1] See, for example, L. Landau and E. Lifshitz, *Physique Statistique*, Moscow (1967).
- [2] M. Apostol and J. E. Fischer, *J. Phys. Chem.*, to appear.
- [3] M. Apostol, C. Goze, F. Rachdi, M. Mehring and J. E. Fischer, *Solid State Commun.*, to appear.
- [4] M. Apostol, *J. Theor. Phys.* **1** (1995).
- [5] M. Apostol, *Synth. Met.*, to appear.