On the Tammann—Rule

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Dedicated to Professor Rüdiger Kniep on the Occasion of his 60th Birthday

Abstract. The validity of Tammann’s rule is related to the fact that the unavoidable thermal generation of point defects leads to defect—defect interactions and finally to a breakdown of the structure. It is shown that the onset of this defect avalanche, which can be estimated by a cube root law, roughly corresponds to the Tammann temperature. The investigation of simple compounds corroborates this picture and also the observation of a critical defect concentration. Examples are given that Tammann’s rule can be used to systematically search for new solid electrolytes.

Keywords: Phase transitions; Thermodynamics; Ion conduction; Defect interaction; Superionic state

Introduction

In the early days of solid state chemistry the so-called Tammann—rule [1] was formulated stating that at temperatures higher than about two thirds of the melting point \( T_m \) solid state materials become reactive [2] (some authors also propose \( 1/2 \) \( T_m \), depending on the properties examined, see e. g. [3]). In the light of a modern mechanistic understanding which is based on the pioneering work of Wagner and Schottky [4], it became clear that the occurrence of solid state reactions in ionic systems being very frequently transport controlled, presupposes the presence of point defects, i.e. the presence of ionic charge carriers. For mass transport to proceed, conductivities of at least two carriers (two ionic species or one ionic and one electronic species) are necessary. So evidently the product of mobility and concentration is decisive. While a correlation between mobility and melting point is difficult to achieve, in this contribution evidence for a correlation between defect concentration and melting point will be given, which is based on a simple model that takes account of Coulombic interaction of point defects [5]. In Ref. [6] empirical arguments have been reported for a critical defect concentration at the melting point. Notwithstanding the fact that such a relation is not directly connected with Tammann’s rule its validity is investigated, too. In view of the fact that the mobilities are not so different in the high temperature zone of interest, we can formulate the Tammann—rule as: At about 2/3 of the melting point, the charge carrier concentration in solids becomes substantial.

Thermal destiny of ionic crystals

At zero Kelvin the equilibrium charge carrier concentration is zero. (In reality a nonzero frozen—in concentration will be realized, not to mention defects induced by effectively charged impurities which we will neglect in the following). Thermal equilibrium necessarily requires the formation of point defects. In primarily Frenkel disordered materials such as \( \text{AgX} \) (\( X = \text{Cl}, \text{Br}, \text{I} \)) this is primarily a finite concentration of interstitial silver ions and silver vacancies; in primarily Schottky disordered materials such as alkaline halides, both cation and anion vacancies prevail [7]. As long as the temperature is low, the concentration is small and the defects will be randomly distributed. Then ideal mass action laws hold with the consequence that the defect concentration (\( x_{\pm} \)) follows a van’t Hoff law (as long as the defect formation parameters \( \Delta H^0, \Delta S^0 \) can be considered as temperature independent)

\[
 x_{\pm,\text{ideal}} = \exp\left(\frac{\Delta S^0}{2R}\right) \exp\left(\frac{\Delta H^0}{2RT}\right)
\]

Hence \( x_{\pm} \) increases steeply with temperature according to Eq. (1) until the defect concentration is so high that the defects perceive each other. The interaction of the two oppositely charged defects is primarily an attractive Coulomb interaction. This attractive interaction reduces the effective formation enthalpy \( \Delta H^0 \) (we ignore effects on \( \Delta S^0 \)) to \( \Delta H^0 - \Delta H'(x_{\pm}) \) [5, 8]. It hence becomes increasingly easier for the next defects to be formed. As a consequence more defects are formed than expected according to the ideal mass action law (i.e. according to the van’t Hoff relation).

In a \( \ln(x_{\pm}) \) vs \( 1/T \) plot an upward bending of the graph occurs. Such deviations are also observed in the temperature graph of the ionic conductivity (see e. g. [9, 10] and references cited in [5]) and in an anomalous increase in specific heat (see e. g. [11]). As there is a positive feedback (more defects lead to even more defects), an avalanche of charge carriers occurs which eventually leads to a phase changes.

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transformation which can be of first or higher order. This process describes the transition to a superionic state within the same structure. In the case of a first order transformation realistically a transition into another solid structure or into the totally molten state occurs. In particular in the case of Schottky disorder, the molten state represents the naturally expected superionic phase. In such cases the transition will occur even at lower temperatures (by ΔT) as the free enthalpy (G) of the real superionic phase is smaller than the free enthalpy of the virtual superionic phase (no structural modification). If this G—difference is large and hence ΔT substantial, it can be that the premelting regime is completely suppressed. The just described process constitutes a universal behavior for simple compounds and predicts at least an upper limit of the disorder temperature whenever the phase does not undergo a structural change before it melts [13]. Of course, in the case of complex crystal structures, these considerations may not be sufficient to completely describe their thermal evolution.

**Cube root model as a simple means for the description of the thermal destiny**

It was shown in previous papers [5, 12, 13] that a cube root law in x± well describes the defect interaction and leads to a satisfactory description of the disorder in simple crystals including the premelting zone; in the case of a higher order transition it may also describe the disorder in the superionic state, while in the case of first order transition only an upper limit for the transition into the superionic state is obtained. The validity of this model was demonstrated for β—AgI which undergoes a transition to the α—AgI phase, for AgCl and AgBr which undergo a transition to the molten state, as well as for PbF2 which undergoes a higher order transition within the fluorite structure [5, 12–15]. In the latter case the conductivity behavior could even be predicted for the superionic state.

The basis of the cube root law is the assumption that the interaction between defects that are more or less randomly distributed can be approximately mimicked by the interaction that a system of the same carrier concentrations perceives in which they all have the same distances. Then it is just necessary to calculate the Madelung energy of a periodically ordered defect structure, the lattice of which is superimposed to the perfect (host material) lattice. In order to avoid misunderstandings we simply refer to this as the “defect lattice” (spanned by the defects) in the following. This directly leads to the implicit formula, Eq. (2), of which yields the x±(T) relation for the whole temperature range (including the superionic state provided the structure is maintained):

\[
\frac{-\Delta H^0 - T\Delta S^0 - Jx_{\pm}^{1/3}}{kT} = \ln \left( \frac{x_{\pm}}{g_x g_v (\alpha_i - x_{\pm})/\alpha_i} \right)
\]

\[\text{(2)}\]

\(g_x, g_v, \alpha_i, \alpha_c\) denote degeneracy and number of available crystallographic sites). The defect interaction parameter J can be traced back to those parameters that determine the electrostatic interaction energy of the defect lattice [12]:

\[J = \frac{4U_{fd}f}{3\varepsilon_0f} \quad \text{(3)}\]

Figure 1 displays the defect concentrations x±(T) calculated from Eqs. (2), (3) for the silver halides (for first- or higher order phase transitions, a vertical step at Tc has to replace the unphysical S-shaped solution of Eq. (2); this new line corresponds to the solution of Eq. (2) with lowest Gibbs energy). If the transition at Tc is of first order as is the case when the modification is altered or the phase melts, the calculated transition temperature is, as already mentioned, to be taken as the upper limit. The fact that in AgCl, AgBr and AgI, Tc is close to the experimental value means that the difference G (virtual high temperature phase) - G (real high temperature phase) is small. In Ref. [5] also a quantitative criterion has been derived based on Eq. (2) which decides upon whether the transition is of first or higher order.

The correlation between defect concentration evolution and melting point forms the basis of our interpretation of Tammann’s rule. Figure 2 shows the increase in x± relative to xideal (calculated without defect interactions according to Eq. (1)). Owing to the steep self—amplified augmentation it does not matter whether we chose \(x_{\pm}/x_{\text{ideal}} = 1.1\) or \(x_{\pm}/x_{\text{ideal}} = 1.01\) as the beginning of the anomalous increase. Moreover, since in this temperature zone all the materials exhibit similar xideal values, we may even chose an absolute value (e.g. \(x_{\pm} = 10^{-4}\)) as a criterion for the onset temperature (it is already qualitatively clear that the onset of the interaction avalanche requires a similar defect concentration, i.e. a similar mean distance, given the small varia-
directly translates into a correlation between $T_m$ and ionic temperature $T_c$, defect molar fraction $x$, and $T_m$, and Figure 3 demonstrates graphically the correlation of the latter quantities. Indeed it is seen that $T_{onset}$ is proportional to $T_m$ with the proportionality constant between 0.5 and 2/3 as proposed by the modified Tammann relation. A better agreement is not to be expected because of the qualitative character of Tammann’s rule. Interestingly, the calculated defect concentrations at the predicted critical temperatures $T_c$ shown in Table 1 are similar and fall in the range of $2 \cdot 10^{-3}$ – $7 \cdot 10^{-2}$. Here the “thermal destiny” outlined above explains the observation of a “critical” defect concentration.

The finding that the correlation between $T_m$ and $x$ directly translates into a correlation between $T_m$ and ionic conductivity is due to the fact that the mobilities of simple compounds are not so different close to the critical temperature. This was shown for fluorites in Ref. [17] with mobilities of $\approx 3 \cdot 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$; it holds also for the silver halides [18] and the alkali halides [19, 20] exhibiting comparable mobilities close to $T_c$. This fact is accepted as an empirical finding in this paper but of course also relies on energetic and entropic reasons. As we face a relation between thermodynamic and kinetic quantities this is more difficult to explain.

The most important quantities for high defect concentrations are of course the defect formation parameters $\Delta H^0$ and $\Delta S^0$. $U_M$ and $f_d/l$ of the defect superlattice will not vary much because for Schottky as well as for Frenkel disorder (to mention the most frequent defect types) cationic and anionic defects are formed in a 1:1 stoichiometric ratio. The influence of $\epsilon_r$ essentially becomes effective through $\Delta H^0$. For a given structure a larger $\epsilon_r$ usually implies a lower defect formation enthalpy $\Delta H^0$ (because the host structure becomes dielectrically softer), which outweighs the decrease in $J$. A weaker influence of $\epsilon_r$ appears via $J$, there the effect is opposite as a high $\epsilon_r$ weakens the defect interactions.

Turning around Tammann’s rule: Search strategy for good ion conductors

If we assume that the molten state is the superionic state of interest (i.e. no superionic solid phase exists, as in the case of Schottky disordered solids) we can state that high defect concentrations imply low melting points. The reversal is not as strict because of the discrepancy between virtual high temperature structure and real structure. Nonetheless, searching for low melting ionic compounds is a powerful search strategy for materials that easily form defects and hence offer the possibility to be good ion conductors. This qualitative tendency is obvious e.g. when we consider the alkali halides AX (variation of the cation in the series LiCl, NaCl, KCl, RbCl, CsCl, NaBr, KBr, RbBr, CsBr, NaI, KI, RbI, CsI), AgI, AgBr, AgCl, PbF$_2$, and CaF$_2$.
NaCl, KCl, RbCl, CsCl or of the anion LiCl, LiBr, LiI). It is also striking that soft, low melting solids such as silver halides, stoichiometric lithium halide-alcohol adducts [21] or alkali triflates [22] exhibit high ionic conductivities. A spectacular example are ionic liquids. Ionic materials such as quartenary amines or imidazolium salts possess a melting point around room temperature and some of them have been recognized to exhibit high conductivities in the solid state at moderate temperatures, see e. g. [23].

Conclusions

Owing to interactions between defects an overexponential increase of defect formation starts typically at a temperature that can be identified with Tammann's temperature. This defect avalanche unavoidably leads to a molten state (if a superionic phase or a phase with different structure is not thermodynamically available), thus connecting melting point and defect concentrations. This behavior forms an explanation of Tammann's rule. As the latter refers to reactivities, i.e. in the diffusion controlled case to conductivities, the validity of the approach presupposes comparable mobilities in the premelting zone, which is indeed the case for many simple materials. If a solid phase undergoes a modification change before it melts, we have to refer to the solid high temperature phase and the picture may change. Finally, we gave examples that, in the case of simple structures, Tammann's rule can be used as a guideline to search for new solid electrolytes.

References

[16] N. H. March, M. P. Tosi, J. Phys. Chem. Solids 1985, 46, 757. Please note: The liquid Madelung factor of 0.73 given in [16] (and incorrectly used in Ref. [13]) refers to a “mean ion diameter” as the relevant length scale, which is slightly smaller than half the lattice constant. The resulting liquid Madelung energy amounts to = 0.9 of $U_M$ (perfect solid). Putting the solid and the liquid to the same length scale thus implies $\xi_d/\xi = 0.9$.