

# On the Tammann–Rule

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*Dedicated to Professor Rüdiger Kniep on the Occasion of his 60<sup>th</sup> 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  $AgX$  ( $X = Cl, Br, I$ ) 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  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$  can be considered as temperature independent)

$$x_{\pm,ideal} = \exp\left(\frac{\Delta S^{\circ}}{2R}\right) \exp\left(-\frac{\Delta H^{\circ}}{2RT}\right) \quad (1)$$

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  $\Delta H^{\circ}$  (we ignore effects on  $\Delta S^{\circ}$ ) to  $\Delta H^{\circ} - |\Delta H^{\circ}(x_{\pm})|$  [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

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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  $\Delta T$ ) 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  $\Delta T$  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.

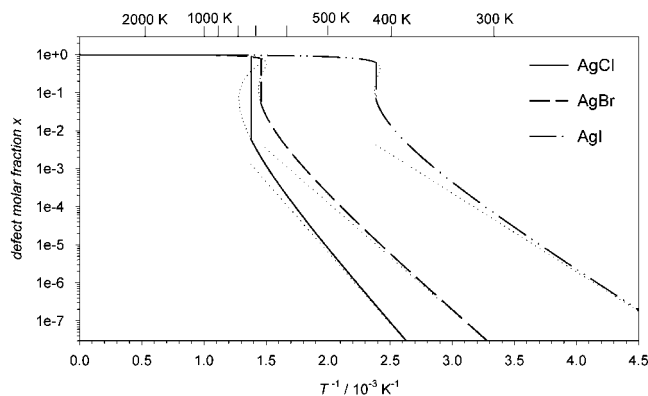
### Cube root model as a simple means for the description of the thermal destiny

It was shown in previous papers [5, 12, 13] that a cube root law in  $x_{\pm}$  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  $\beta$ -AgI which undergoes a transition to the  $\alpha$ -AgI phase, for AgCl and AgBr which undergo a transition to the molten state, as well as for PbF<sub>2</sub> 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), the solution of which yields the  $x_{\pm}(T)$  relation for the whole temperature range (including the superionic state provided the structure is maintained):

$$-\frac{\Delta H^0 - T\Delta S^0 - Jx_{\pm}^{1/3}}{kT} = \ln\left(\frac{x_{\pm}^2}{g_i g_v (\alpha_i - x_{\pm}) (\alpha_v - x_{\pm})}\right) \quad (2)$$

( $g_i$ ,  $g_v$ ,  $\alpha_i$ ,  $\alpha_v$ , denote degeneracy and number of available crystallographic sites). The defect interaction parameter



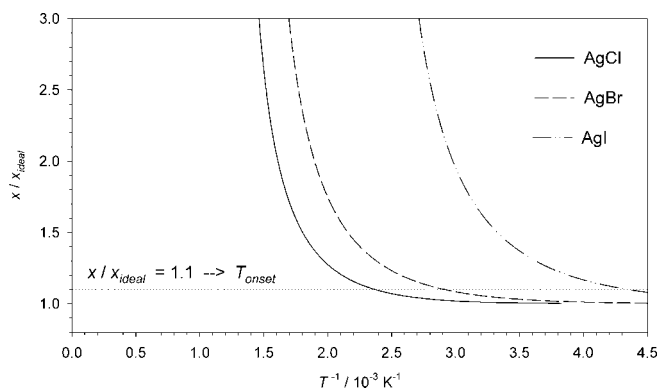
**Figure 1** Molar fractions of Frenkel defects calculated according to eq. (2). Dotted straight lines indicate ideal defect concentrations in the absence of defect interactions.

$J$  can be traced back to those parameters that determine the electrostatic interaction energy of the defect lattice [12]:  $U_M$  (Madelung energy of a perfect lattice with same cation/anion stoichiometry as the defect lattice), dielectric constant  $\epsilon_r$  and  $f_d/f$  (ratio of the Madelung constants of a crystalline phase and the value for the corresponding melt,  $f_d/f \approx 0.9$  [16])

$$J = \frac{4U_M f_d}{3\epsilon_r f} \quad (3)$$

Figure 1 displays the defect concentrations  $x_{\pm}(T)$  calculated from Eqs. (2), (3) for the silver halides (for first- or higher order phase transitions, a vertical step at  $T_c$  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  $T_c$  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,  $T_c$  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  $x_{\pm}$  relative to  $x_{\text{ideal}}$  (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  $x_{\text{ideal}}$  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-



**Figure 2** Ratio of defect molar fraction  $x_{\pm} / x_{\text{ideal}}$  with and without defect interactions. The dotted line marks the chosen criterion  $x_{\pm} / x_{\text{ideal}} = 1.1$  for determination of the onset temperature.

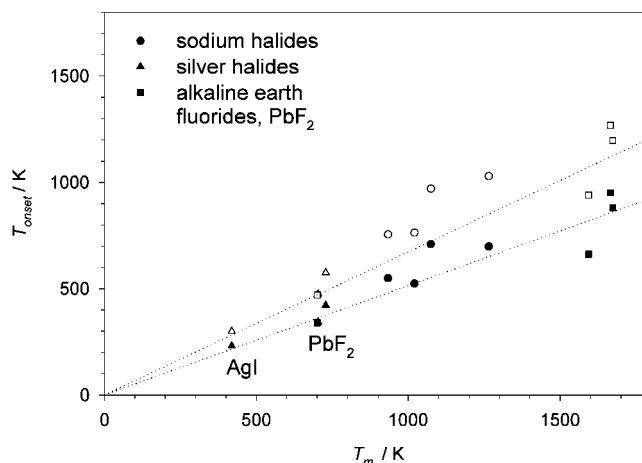
tions in  $\epsilon_r$  and in  $f_d/f$ ). Table 1 gives  $T_c$  as well as  $T_{\text{onset}}$  together with  $T_m$ , and Figure 3 demonstrates graphically the correlation of the latter quantities. Indeed it is seen that  $T_{\text{onset}}$  is proportional to  $T_m$  with the proportionality constant 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  $x_{\pm}$  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 mo-

**Table 1** Melting temperature  $T_m$  (\* or superionic phase transition for AgI,  $\text{PbF}_2$ ), onset temperature  $T_{\text{onset}}$  ( $x_{\pm}/x_{\text{ideal}} = 1.1$ ), critical temperature  $T_c$ , defect molar fraction  $x_{\pm}$  at  $T = T_c$ , and references for defect formation parameters of selected halides. \*\*  $T_c$  for the fluorite materials exhibiting only a diffuse phase transformation is estimated graphically from plots of  $x_{\pm}$  versus  $1/T$ .

Please note: for the fluorite materials, the defect lattice (anion vacancies and interstitials) has 1:1 stoichiometry and is thus approximated by a NaCl structure with appropriate lattice constant

	$T_m/\text{K}$	$T(x_{\pm}=10^{-4})$	$T(x_{\pm}=10^{-6})$	$T(x_{\pm}/x_{\text{id}}=1.1)$	$T_c/\text{K}$	$x_{\pm}(T_c)$	Ref.
NaF	1265	1030	791	699			[24]
NaCl	1074	971	751	710	1347	0.063	[24]
NaBr	1020	764	587	525	942	0.0025	[24]
NaI	933	756	580	550	1083	0.075	[24]
AgCl	728	576	448	422	727	0.0062	[5]
AgBr	703	475	362	343	687	0.056	[5]
AgI	419*	300	240	230	419	0.071	[5]
$\text{CaF}_2$	1665	1268	937	951	2000**		[25]
$\text{SrF}_2$	1673	1196	869	879	2000**		[25]
$\text{BaF}_2$	1593	940	686	661	1550**		[25]
$\text{PbF}_2$	700*	471	358	339	680**		[5]



**Figure 3** Plot of onset temperature of defect interaction versus experimental melting temperature (for AgI and  $\text{PbF}_2$ : versus experimental transformation temperature to superionic phase). Solid symbols: relative criterion  $x_{\pm} / x_{\text{ideal}} = 1.1$ ; open symbols: absolute criterion  $x_{\pm} = 10^{-4}$ . The dotted lines correspond to  $2/3 T_m$  and  $1/2 T_m$ , respectively.

bilities 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  $f_d/f$  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 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 quaternary 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

- [1] G. Tammann, *Lehrbuch der Metallkunde*, 4. ed., Verlag Voss, Berlin 1929.
- [2] K. Hauffe, *Reaktionen in und an festen Stoffen*, Springer, Berlin 1966, p. 814.
- [3] D. J. M. Bevan, J. P. Shelton, J. S. Anderson, *J. Chem. Soc.* **1948**, 1729.
- [4] C. Wagner, W. Schottky, *Z. Phys. Chem.* **1930**, *B11*, 163; C. Wagner, *Z. Phys. Chem.* **1936**, *B32*, 447.
- [5] N. Hainovsky, J. Maier, *Phys. Rev.* **1995**, *B 51*, 15789.
- [6] K. Shahi, W. Weppner, A. Rabenau, *Phys. Status Solidi* **1986**, *a93*, 171.
- [7] F. A. Kröger, *Chemistry of Imperfect Crystals*, North-Holland, Amsterdam, 1964.
- [8] R. A. Hubermann, *Phys. Rev. Lett.* **1974**, *32*, 1000.
- [9] C. E. Derrington, A. Lindner, M. O'Keefe, *J. Solid State Chem.* **1975**, *15*, 171.
- [10] J. K. Aboagye, R. J. Friauf, *Phys. Rev.* **1975**, *B 11*, 1654.
- [11] W. Schröter, J. Nölting, *J. Phys. Colloq. C6* **1980**, *41*, 20.
- [12] N. Hainovsky, J. Maier, *Solid State Ionics* **1995**, *76*, 199.
- [13] J. Maier, W. Münch, *Z. Anorg. Allg. Chem.* **2000**, *626*, 264.
- [14] F. Zimmer, P. Ballone, J. Maier, M. Parrinello, *J. Chem. Phys.* **2000**, *112*, 6416.
- [15] F. Zimmer, P. Ballone, M. Parrinello, J. Maier, *Solid State Ionics* **2000**, *127*, 277.
- [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  $\approx 0.9$  of  $U_M$  (perfect solid). Putting the solid and the liquid to the same length scale thus implies  $f_d/f \approx 0.9$ .
- [17] J. Schoonman, *Solid State Ionics* **1980**, *1*, 121.
- [18] P. Müller, *Phys. Status Solidi* **1965**, *12*, 775.
- [19] M. Beniere, M. Chemla, F. Beniere, *J. Phys. Chem. Solids* **1976**, *37*, 525.
- [20] H. Hoshino, M. Shimoji, *J. Phys. Chem. Solids* **1967**, *28*, 1169.
- [21] R. Kniep, W. Welzel, W. Weppner, A. Rabenau, *Solid State Ionics* **1988**, *28*, 1271.
- [22] M. Pompetzki, L. van Wüllen, M. Jansen, *Z. Anorg. Allg. Chem.* **2004**, *630*, 484.
- [23] H. A. Every, A. G. Bishop, D. R. MacFarlane, G. Orädd, M. Forsyth, *Phys. Chem. Chem. Phys.* **2004**, *6*, 1758.
- [24] M. W. Roberts, J. M. Thomas (eds.), *Surface and defect properties of solids*, vol. 6, The Chemical Society, 1977.
- [25] A. V. Chadwick, *Solid State Ionics* **1983**, *8*, 209.