II-2.3 Schottky defects form when cation-anion pairs are missing from their respective lattice sites (Fig. II-4a) leading to equal number of cation and anion vacancies. Schottky defects occur often in alkali halide crystals. As the volume of the crystal remains unchanged but the mass is now lower, these defects lead to a decrease in the density of the crystal. The defects can also be visualized as arising due to the migration of the cation-anion pair to the crystal surface. The defect population is again given by:

 $n = Ne^{-E_S/2k_BT}$  (the factor of 2 arises due to the pair of ions involved)

- Density of a crystal can be estimated from the unit cell information. An example:
  - Consider a salt M<sup>+</sup>X<sup>-</sup> (molecular weight = 74.6 g mol<sup>-1</sup>) with an fcc lattice and the distance between M<sup>+</sup> and X<sup>-</sup> = 0.32 nm.
  - Number of M'X' in the conventional unit cell = 4; unit cell length = 0.64 nm.
  - O Density,  $\rho = \frac{4 \times 74.6 \times 10^{-3}}{6.023 \times 10^{23} \times (0.64 \times 10^{-9})^3} = 1.890 \times 10^3 kg m^{-3}$
- □ If the above crystal has 0.1% Schottky defects, the density will be:
  - $\rho_{def.\ cryst.} = 1.89 \times 10^3 \times \frac{99.9}{100} = 1.888 \times 10^3 kgm^{-3}$
- II-2.4 Frenkel defects form when an ion (often the cation) migrates from the lattice site where it is expected to be, to an interstitial position (Fig. II-3b). These occur often in relatively open structures with large interstitial spaces. Silver halides are typical crystals in which Frenkel defects are found. As the vacancy is compensated by the interstitial ion, Frenkel defects lead to no change in the density of the crystal. The defect population is given by:

 $n = \sqrt{(NN_t)}e^{-E_x/2k_BT}$  (N<sub>t</sub> is the number of interstitial sites)

(m)	Schottky pair	(b)	Frenkel defect							
00	000000	0 0	@ C	3 (	9 0	0	0	0	0	(3)
00	@ 0 0 0 lo c	0 0	0 0	3 (	3 O	0	0	0	0	0
00	000000	0 0	(O) (	9 0	9 Q	0	0	0	0	0
00	000000	0 0	(O) (	<b>3</b> (	9 G	0	0	0	0	G
00	000000	0 0	0 0	3 0	9 0	0	0	0	0	G
00	000000	0 0	00	3 0	9 O	0	0	0	0	G
00	000000	0 0	(O) (	2 0	20	0	0	$\odot$	0	Œ
00	000000	0 0	0 0	3 0	9 G	0	0	0	0	G
00	000000	0 0	@ (	9 0	<b>O</b>	0	0	0	0	Œ

Figure II-3. (a) Schottky and (b) Frenkel defects; circles represent the lattice points and \* and - the ions that form the basis.

# **Problems Of Nonstoichiometry**

A.I. Gusev, A.A. Rempel, A.J. Magerl

#### **Problems Of Nonstoichiometry:**

Problems of Nonstoichiometry John Stuart Anderson, 1970 Problems of Nonstoichiometry Albrecht Rabenau, 1970 Disorder and Order in Strongly Nonstoichiometric Compounds A.I. Gusev, A.A. Rempel, A.J. Magerl, 2013-03-09 long to understand that the phenomena associated with the redistribution of interstitial atoms and structural vacancies in non stoichiometric compounds represent an excellent model of analogous phenomena arising in solid state systems with mutual substitution of components Therefore methods of analysis and description proposed and developed for nonstoichiometric compounds are applicable to a number of systems with substitutional disorder In 1980 when we embarked on this work ordering in nonstoichiometric compounds was assumed to be a rare and accidental effect which hardly deserved close attention Now many people understand that ordering represents a general regular phenomenon in all non stoichiometric compounds Ordering effects which were not even mentioned or were referred to as something insignificant and negligible just 20 years ago proved to be numerous and comparable in magnitude with the change of properties in the whole homogeneity interval of non stoichiometric compounds Phase diagrams of binary systems of transition metals with carbon and nitrogen which remained unchanged from the time they were plotted in 1950 60s and containing one or two nonstoichiometric compounds were enriched with many ordered phases Unfortunately the accumulated experimental and theoretical knowledge has not so far been disseminated widely **Ternary and Multinary Compounds** R.D Tomlinson, A.E. Hill, R.D Pilkington, 2020-10-28 Multinary compounds are now used in a wide range of devices including photovoltaic solar cells light emitters and detectors and piezoelectric actuators Ternary and Multinary Compounds provides an interdisciplinary forum for scientists and engineers working on fundamental and applied aspects of these materials. The volume focuses on optoelectronic properties electronic band structure charge carrier transport optical and magnetic properties and superconductivity It includes chapters on the research and development of new techniques and novel materials such as laser Nonstoichiometric Compounds Ronald Ward, American Chemical Society. Division ablation deposition and ferroelectrics of Inorganic Chemistry, 1963 Non-Stoichiometric Oxides of 3d-Metals Andrzej Stokłosa, 2015-03-18 In the present work in Part I new elements widening the bases of the defects theory are shown particularly this work discusses the mechanism of the formation of defects as a result of elementary processes the work also presents a description of the equilibrium state by one equation taking into account the concentrations of defects and their changes during the process of reaching the equilibrium The equation relates the concentrations of defects dependent on the standard Gibbs energies of their formation with the equilibrium pressure of oxygen The obtained relations and the discussion have lead to the development of a method for determination of complete diagrams of concentrations of the point defects which allows taking into account the minority defects Part II presents the results of the calculations of the diagrams of point defects concentrations for a series of pure and doped oxides of transition metals 3d with different composition M O ratio

crystallographic structure and point defects structure A critical analysis of the results of the studies of the deviation from the stoichiometry and the electrical conductivity obtained so far by most research groups has been also performed A new interpretation of these results concerning concentrations and types of ionic defects present has been performed and the mobility of electronic defects and its dependence on the temperature and oxygen pressure have been determined Metals Abstracts ,1981 Problems of nonstoichiometry, ed: A. Rabenau, contributors: J.S. Anderson , Thermodynamics and Stability Limits of Mixed Oxides in the Co-Fe-Mn-O System at 1200C Ramesh Subramanian,1993 Defects and Diffusion in Ceramics - An Annual Retrospective VII David Fisher,2005-09-30 This seventh volume in the series covering the latest results in the field includes abstracts of papers which appeared between the publication of Annual Retrospective VI Volumes 226 228 and the end of July 2005 journal availability permitting The Chemistry of Extended Defects in Non-metallic Solids LeRoy Eyring, Michael O'Keeffe, 1970 Römpps Chemie-Lexikon Otto-Albrecht Neumüller, 1972

Memoirs of the Institute of Scientific and Industrial Research, Osaka University ,1978 **CFI** .1986 Research and Standards ,1972 Ceramic Microstructures Antoni P. Tomsia, Andreas M. Glaeser, 2012-12-06 This volume titled Proceedings of the International Materials Symposium on Ce ramic Microstructures Control at the Atomic Level summarizes the progress that has been achieved during the past decade in understanding and controlling microstructures in ceram ics A particular emphasis of the symposium and therefore of this volume is advances in the characterization understanding and control of micro structures at the atomic or near atomic level This symposium is the fourth in a series of meetings held every ten years devoted to ceramic microstructures The inaugural meeting took place in 1966 and focussed on the analysis significance and production of microstructure the symposium emphasized the need for and importance of characterization in achieving a more complete understanding of the physical and chemical characteristics of ceramics A consensus emerged at that meeting on the critical importance of characterization in achieving a more complete understanding of ceramic properties That point of view became widely accepted in the ensuing decade The second meeting took place in 1976 at a time of world wide energy shortages and thus emphasized energy related applications of ceramics and more specifically microstructure property relationships of those materials The third meeting held in 1986 was devoted to the role that interfaces played both during processing and in influencing the ultimate properties of single and polyphase ceramics and ceramic metal systems **Growth of Crystals from the Vapour** M. M. Faktor, I. Garrett, 1974

Nonstoichiometric Oxides O. Toft Sørensen,1981 Inorganic Materials ,1989 Russian Journal of Physical Chemistry ,2000

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