VARIATION OF F-CENTER CONCENTRATION IN DILUTE K-KCL SOLUTION: COMPARISON OF AN OPTICAL STUDY WITH THERMODYNAMIC PREDICTION

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Abstract - We have measured the concentration of liquid F-centers by optical absorption in K_xKCl_{1-x} solutions at 790 °C over a wide range of compositions up to a metal mole fraction $x = 0.01$. The composition has been accurately controlled by coulometric titration in situ. These results are compared with the predictions of the F-center concentration as determined from metal activity measurements using a thermodynamic electron defect model. Good agreement is found between these separate data sets for a variation of composition by two orders of magnitude.

1. Introduction

The F-center (colour center) is the first and best studied electronic defect species in solid state physics and chemistry. It is described as an electron localized at an anion vacancy /1/. Spectroscopically the crystalline F-center has been characterized in detail by various methods during more than six decades, going back to the pioneering work of Pohl's school in Göttingen - for reviews see /2/, /3/-. However, its thermodynamic properties like chemical potential or reaction enthalpy for the equilibrium F-center - colloid and the correlation between thermodynamic and electronic properties are less well studied. This is mainly due to the fact that the phase width of the metal doped alkali halides is very narrow and thus allows only a small equilibrium concentration of F-centers of e.g. 10^{18} cm^{-3} at 600 °C /4/. In addition, crystalline F-centers in most cases have been produced by additive colouration through the vapour phase and the colloids have been formed by quenching, a non equilibrium state. Markham /3/, p. 62, admires this as "an art and not a science". As a matter of fact, a variety of electronic defect equilibria has been considered in solid state chemistry - see e.g. Kröger /5/ -. But in many cases the experimental verification in solids is limited to a relatively narrow concentration or activity range due to the phase behaviour or experimental difficulties at the necessary high temperatures.

In alkali metal - alkali halide melts the situation is different. Here a complete miscibility in thermal equilibrium exists at elevated temperatures of the order of 10^3 K /6/. Spectroscopic and theoretical studies strongly indicate that on the salt-rich side of these solutions F-center like states form - for a recent review see /7/. Deviations from this may be considered for M-NaX and M-LiX systems /8/, /9/. In connection with the considerations on electronic defect models above these systems offer the particular attraction that the corresponding thermodynamic equilibria can be followed over a wide range of composition and corresponding thermodynamic metal activities where clearly non ideal behaviour prevails.

In this study emphasis is given to this point. The concentration of F-centers in liquid K_xKCl_{1-x} has been determined optically for a variation of metal mole fraction x , $10^{-4} \leq x \leq 10^{-2}$, where x has been varied in situ by coulometric titration. These data are compared with the corresponding predictions of an electron defect model which uses as input data measured metal activities /10/, /11/.

2. Experimental

In order to control and vary in situ the composition of the K_xKCl_{1-x} melt accurately, we have combined an EMF-cell with the optical cell as sketched in Fig. 1. The EMF-cell allows coulometric titration of the K-metal according to the following reaction:

This technique using CaF_2 as a solid electrolyte was first employed by Egan on liquid alloy studies /12/. Details of the operation of this method and the necessary corrections to determine the metal amount dissolved in the molten salt are also described in two previous papers where it has been applied to metal molten salt solutions /13/, /14/.

For the following only the principle of titration with this EMF-cell is of interest: for a given EMF the K-metal activity in the double salt $KCaF_3$ is fixed, and via equilibration through the vapour phase the same activity is present in the molten salt. For further details reference is given to /13/, /14/. The optical part of the cell in principle consists of two circular sapphire windows sealed vacuum tight with a thin Ta- or Fe-wire defining the thickness of the liquid salt film of about 20 μm . Further details of the optical cell and measurements are described in /15/. Two comments on this experiment are of importance. On titration of the metal, equilibration in the optical film is fast, of the order of minutes. However, so far we did not succeed to keep the concentration constant over a long period of several hours. This is easily detected by the optical extinction and changing EMF. There are either electronic leakage currents which discharge the cell slowly - due, e.g., to impurity deposition on CaF_2 or reactions at high temperatures - or the cell is not absolutely tight. So in

the present experiments we were not yet able to count the charge reliably enough to determine directly the amount of metal dissolved; but we set a constant potential E when taking the spectra which defines the metal activity a_K via the Nernst equation. Through these activities the mole fractions x have been determined from the thermodynamic measurements of $a_K(x) / 11\%$.

Fig. 1: High temperature optical absorption cell combined with an EMF-cell for in situ coulometric titration.

3. Results and Discussion

Typical absorption bands of the F-center in liquid K_xKCl_{1-x} at 790 °C are presented in Fig. 2 for various EMF-values ranging from 150 mV to - 10 mV. The spectra shown have been corrected for the absorption background measured on the pure molten salt before titration. An uncertainty in the background may be due to slight corrosion of the sapphire windows. This has been checked and corrected by measurements on the pure salt after taking out the metal by titration. The temperature has been calibrated relative to the melting point of the pure salt by observation of the fundamental absorption edge of the salt. The absolute accuracy is found to be ± 5 °C. The spectra have been reproduced at various titrations in the same run and with separate fillings in different experiments to better than 0.1 extinction units at the same EMF.

Fig. 2: Selection of optical absorption spectra of K_xKCl_{1-x} at 790 °C for various titrations with increasing and decreasing EMF and corresponding x -values $0.0007 \leq x \leq 0.0034$. Plotted is the extinction vs photon energy in eV. Increasing EMF-values correspond to decreasing extinctions.

In Fig. 2 it is apparent that the width of the absorption band at half maximum does not change with composition. So the height of the band, or the absorption constant at the band maximum, K , is directly proportional to the concentration of F-centers, n_f . The K -values have been determined with Beer's law from the extinctions. The film thickness has been determined after the experiment by measuring the thickness of the sealing wire with a light section microscope. These data of K/cm^{-1} are plotted in Fig. 3 as a function of K -activity, a_K . Here the a_K -values have been determined from the experimental EMF via the Nernst-equation, i.e.

$$a_K = \exp \left(- \frac{(E-E_0)F}{RT} \right) \quad (2)$$

where F is the Faraday constant, R is the gas constant, and E_0 is the EMF at saturation of the double salt - see /13/. As can be seen in Fig. 3 the reproducibility of data from different experiments - circles in comparison with triangles - is very good.

Fig. 3: Absorption constant, K , at the band maximum as a function of K-metal activity, a_K , of K_xKCl_{1-x} at 790 °C. Comparison of results from different optical experiments (symbols O and Δ) with the prediction of thermodynamic defect model (full line). The concentration n_F of F-centers (right hand scale) has been determined from the spectra via the corresponding K -values using the Smakula equation - see e.g. /3/ -. For the n_F -data from thermodynamics see text.

However, the most interesting observation is that the concentration of F-centers (proportional to K/cm^{-1}) over almost two orders of a_K follows a straight line. This exactly is the prediction of the thermodynamic defect model, which is described in detail in /12/ and /13/. It considers with increasing metal concentration the formation of electrons - which may be spread in localized states in the mobility gap -, F-centers, and higher aggregated states. Taking into account the corresponding equilibria which define the equilibrium constants K_i one finds /13/:

$$n_F = (K_{\text{VII}}^{-1} / a_K^I) \cdot a_K \cdot (N_A / V_m) \quad (3)$$

where K_{VII}^{-1} is the equilibrium constant for the ionisation of the F-center and the constant a_K^I is the activity where the concentrations of electrons and F-centers are equal, N_A is the Avogadro constant and V_m the molar volume. The constant K_{VII}^{-1} and a_K^I have been determined

from fitting the model equations to measured activities /11/ and measured electronic conductivities /16/. So these constants define the slope of n_F vs a_K , which is presented by the straight line in Fig. 3. If one plots K or n_F versus x clear deviations from a linear behaviour are observed, as is demonstrated in Fig. 4. This is not surprising as ideal behaviour does not hold any more at these high activities. In the solid, where the maximum F-center concentration in thermal equilibrium is much lower, a linear relation between n_F and x_K over three orders of magnitude has been found - see e.g. /4/ -.

Fig. 4: Concentration of F-centers, n_F , versus mole fraction x of liquid K_xKCl_{1-x} at 790 °C. Symbols correspond to optical determination, full line to thermodynamic model. For the determination of n_F via the Smakula equation /3/ the oscillator strength is taken as 1.

In summary we may conclude that the optically determined concentration dependence of F-centers presented here for K_xKCl_{1-x} melts quantitatively agrees with the predictions of a thermodynamic electronic defect model based on measured activities. The agreement comprises both the linear dependence of n_F vs a_K and the slope.

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