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Chemical Diffusion and Defect Mobility in Nonstoichiometric Manganous Sulfide

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The chemical diffusion coefficient in nonstoichiometric manganous sulfide, $Mn_{1-y}S$, was measured as a function of temperature (1073–1373 K) and sulfur pressure (10^{-2}–10^3 Pa) using the electrical conductivity reequilibration kinetic method. It has been shown that the mobility of doubly ionized cation vacancies in $Mn_{1-y}S$ is independent of their concentration and can be characterized by the following empirical relationship describing the temperature dependence of the defect (vacancy) diffusion coefficient:

$$D_V = 1.3 \times 10^{-2} \exp\left(-\frac{76.4 \pm 0.5\ \text{kJ/mol}}{RT}\right).$$

Using these data, the activation entropy and enthalpy of defect migration in $Mn_{1-y}S$ have been calculated: $\Delta S_m = 10.4$ J/mol deg and $\Delta H_m = 76.4 \pm 0.5$ kJ/mol. © 1992 Academic Press, Inc.

Introduction

The high temperature form of manganous sulfide, α-MnS, is the only stable compound in the Mn–S system above 473 K (*1*, *2*). In contrast with manganous oxide, MnO, (*3*, *4*) and many other transition metal sulfides, this compound shows very small deviations from stoichiometry and thereby defect concentration, being even smaller than those of manganous oxide, MnO, (*3*, *4*).

It has been shown (*5*, *6*) that over the major part of the phase field, corresponding to higher sulfur activities, α-MnS is a metal deficit p-type semiconductor with the predominant defects being double ionized cation vacancies and electron holes ($Mn_{1-y}S$). The concentrations of these defects as a function of temperature and sulfur activity can be described by the following empirical equation (*6*):

$$[V''_{Mn}] = \tfrac{1}{2}[h^{\cdot}] = 4.77 \times 10^{-2} p_{S_2}^{1/6} \exp\left(-\frac{41.5\ \text{kJ/mol}}{RT}\right). \tag{1}$$

However, the mobility of point defects in $Mn_{1-y}S$ has not been determined so far.

The aim of the present paper is an attempt to get preliminary information on this problem by determining the chemical diffusion coefficient in the discussed sulfide as a function of temperature and sulfur activity.

Chemical Diffusion Coefficient

The chemical diffusion is a process of migration of defects under their concentration

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gradient (*7–9*). In the case of nonstoichiometric oxides and sulfides, the chemical diffusion coefficient can be obtained from thermogravimetric or electrical conductivity measurements of a given sample as a function of time when going from one thermodynamic equilibrium state to another.

In the case of manganous sulfide, the application of the thermogravimetric method is problematic, as the maximum deviations from stoichiometry of $Mn_{1-y}S$, even at very high temperatures (~1473 K) are rather low ($y < 10^{-3}$). Consequently, the determination of mass changes of a given specimen as a function of time in a sulfur vapor environment is virtually impossible with acceptable accuracy. However, the reequilibration kinetics of manganous sulfide can be followed with sufficient accuracy using the electrical conductivity method (*10, 11*), because the concentration of electron holes in $Mn_{1-y}S$ changes proportionally with the concentration of cation vacancies (Eq. (1)). Assuming that the mobility of electron holes remains independent of their concentration (*12–15*), it is evident that these two techniques—gravimetric and electrical conductivity methods—should yield the same results.

To obtain the chemical diffusion coefficient from electrical conductivity data for a flat rectangular sample, two appropriate solutions of Fick's second law were used (*16*):

1. For the semi-infinitive case, i.e., short reequilibration times, where $\tilde{D}t/a^2 < 0.25$ ($2a$ is the sample thickness, and t is time). The solution is

$$\left(\frac{\Delta\sigma_t}{\Delta\sigma_\infty}\right)^2 = \frac{4\tilde{D}t}{\pi a^2}, \qquad (2)$$

where $\Delta\sigma_t$ is the change of the electrical conductivity after time t, and $\Delta\sigma_\infty$ denotes the total change of σ when the new equilibrium state is established.

2. For the finite case, i.e., long reequilibration times, where $\tilde{D}t/a^2 > 0.15$:

$$\left[1 - \left(\frac{\Delta\sigma_t}{\delta\sigma_\infty}\right)\right] = \frac{8}{\pi^2}\exp\left(-\frac{D\pi^2 t}{4a^2}\right). \qquad (3)$$

It follows from these two relationships that for short reequilibration times the kinetics of this process should be parabolic and in later stages the logarithmic behavior should be observed.

It should be noted that Eqs. (2) and (3) are valid for oxidation and reduction runs, since the boundary conditions in the solutions of the Fick's second law are identical for both cases.

Results and Discussion

The starting materials for the electrical conductivity measurements have been obtained by complete sulfidizing of the spectrally pure manganese plates (10 × 1 × 0.1 mm) at 1373 K in pure sulfur vapor at a pressure of 10^3 Pa. The sulfide was then powdered and cold-pressed (1000 kg/cm^2) to obtain rectangular specimens (35 × 7 × 5 mm). These were subsequently annealed for 150 hrs at 1373 K in sulfur vapor ($p_{S_2} = 10^3$ Pa) in order to obtain the dense and coarse-grained material. It has been found that after such a treatment the density of the α-MnS samples was higher than 98% with an average grain size of 1 mm. The samples were polished using Al_2O_3 powder to obtain mirror-like surfaces.

The electrical conductivity measurements have been performed using the conventional four-probe AC method at temperatures ranging from 1073 up to 1373 K and sulfur pressures 10^{-2}–10^3 Pa. In order to determine the dependence of the defect mobility on the concentration, the conductivity relaxation curves were obtained for small steps in p_{S_2}, traversing the phase field of $Mn_{1-y}S$. In every experiment the sample was first equilibrated at a certain partial

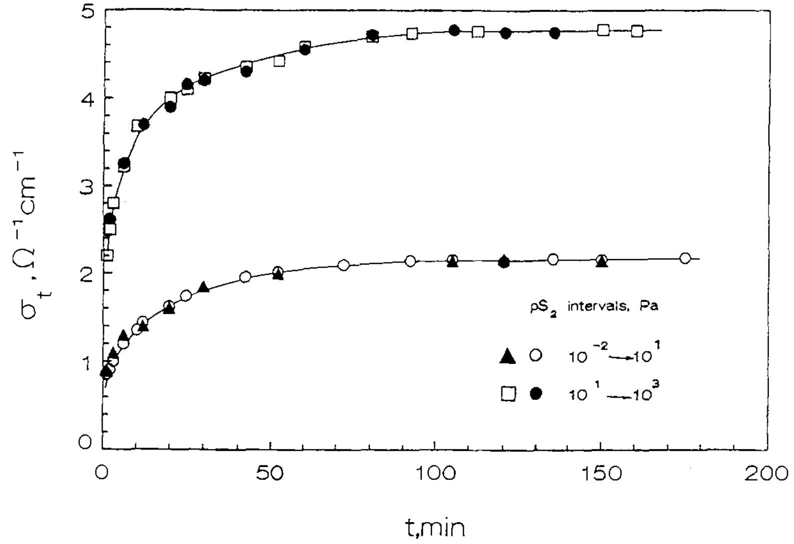

FIG. 1. Reequilibration kinetic curves for two different pressure intervals and four different samples for $Mn_{1-y}S$.

pressure of sulfur vapor and temperature. A step change in p_{S_2} was then created, and electrical conductivity was recorded continuously until no further observable conductivity changes occured, (i.e., sample in equilibrium with the new atmosphere). The apparatus and the details of the experimental procedure were described elsewhere (*17, 18*).

Figure 1 shows the typical oxidation curves obtained at 1273 K for two different pressure intervals. As can be seen, the reproducibility of the data was excellent. Figure 2 illustrates the kinetics of conductivity changes determined at several temperatures during the early stages of reequilibration. In agreement with Eq. (2), the straight lines were obtained in a parabolic plot, enabling the chemical diffusion coefficient to be calculated from the slope of these lines using Eq. (2). Figure 3, in turn, shows the results in a semilogarithmic plot obtained in the later stages of the relaxation process (long-term experiments). As can be seen, again straight lines were obtained in agreement with Eq. (3). The analogous results were obtained at other temperatures and different pressure intervals.

Using all these data, the chemical diffusion coefficient has been calculated as a function of temperature and equilibrium sulfur pressure through Eqs. (2) and (3). The

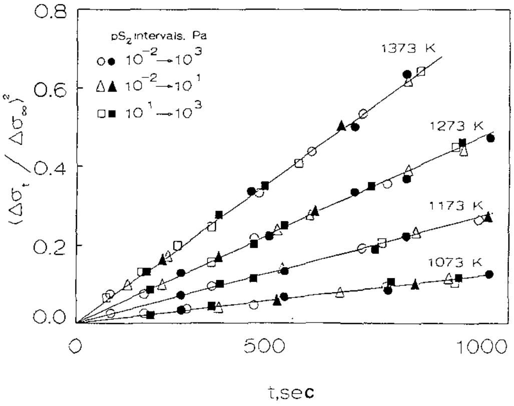

FIG. 2. Parabolic plot of early stages of conductivity change kinetics for $Mn_{1-y}S$.

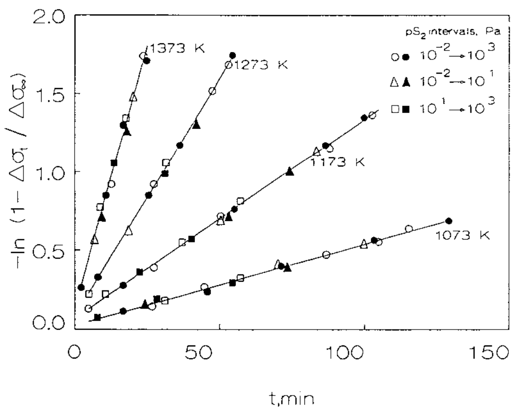

FIG. 3. Semilogarithmic plot of later stages of conductivity change kinetics for $Mn_{1-y}S$.

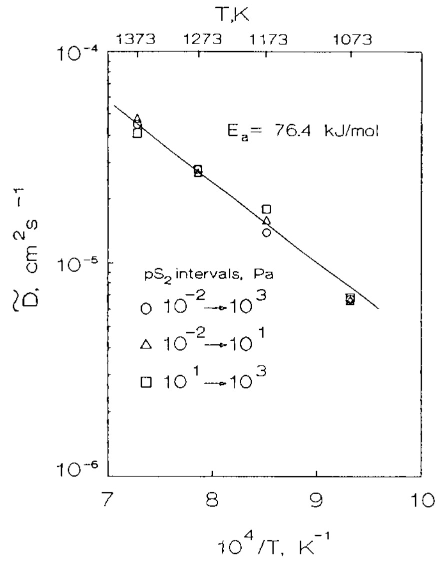

FIG. 5. Temperature dependence of the chemical diffusion coefficient in $Mn_{1-y}S$ for several sulfur pressures (Arrhenius plot).

results of these calculations are collected in Fig. 4. Two important conclusions can be drawn from these plots. First, calculated diffusivities from short- and long-term experiments are virtually the same, which clearly indicates that the rate-determining step in the overall reequilibration kinetics of $Mn_{1-y}S$ is the solid-state diffusion. Thus, the fundamental assumption of the method is fulfilled. Second, it follows from Fig. 4 that the chemical diffusion coefficient in $Mn_{1-y}S$ does not depend on sulfur pressure and thereby on defect concentration. The temperature dependence of this coefficient can, then, be represented by a single plot for all sulfur pressures, as illustrated in Fig. 5. As expected, this dependence is a linear function in the Arrhenius system of coordinates, enabling the calculation of the activation energy of the chemical diffusion and the expression of the chemical diffusion coefficient for $Mn_{1-y}S$ by the following empirical equation:

$$\tilde{D}_{MnS} = 3.9 \times 10^{-2} \exp\left(-\frac{76.4 \pm 0.5\ \text{kJ/mol}}{RT}\right). \qquad (4)$$

The fact, that the chemical diffusion coefficient in a given solid is independent of its composition does not imply directly that the same holds for the defect mobility. The defect diffusion coefficient, D_d, cannot be determined directly from nonequilibrium thermodynamical experiments, but it can

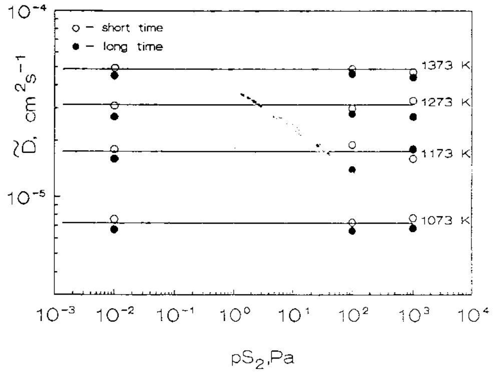

FIG. 4. Pressure dependence of the chemical diffusion coefficient in $Mn_{1-y}S$ for several temperatures (log–log plot).

readily be calculated if the chemical diffusion coefficient and the dependence of defect concentration are known. All of these three important quantities are interrelated by the equation, which for the case under discussion assumes the form

$$D_V = 2\tilde{D}_{\mathrm{MnS}}\left(\frac{d\ln[V''_{\mathrm{Mn}}]}{d\ln p_{S_2}}\right), \qquad (5)$$

where D_V denotes the vacancy diffusion coefficient. As the concentration of cation vacancies in $Mn_{1-y}S$ is a simple power function of sulfur activity (Eq. (1)), from the Eq. (5) it follows clearly that the defect diffusion coefficient is pressure independent. From Eq. (1) it follows that the differential in Eq. (5) is equal to $\frac{1}{6}$, and consequently Eq. (5) reduces to the following simplified form, enabling the defect diffusion coefficient to be calculated from chemical diffusion data:

$$D_V = \tfrac{1}{3}\tilde{D}_{\mathrm{MnS}}. \qquad (6)$$

According to Eq. (4) one obtains finally the empirical relationship describing the vacancy diffusion coefficient in metal deficient manganous sulfide as a function of temperature,

$$D_V = 1.3 \times 10^{-2} \exp\left(-\frac{76.4 \pm 0.5\ \mathrm{kJ/mol}}{RT}\right) \qquad (7)$$

The temperature dependence of the defect diffusion coefficient for simple metal oxides and sulfides is described by the theoretical equation (*7, 8*)

$$D_V = \alpha a_0^2 \kappa \nu \exp\left(\frac{\Delta S_m}{R}\right) \exp\left(-\frac{\Delta H_m}{RT}\right) \qquad (8)$$

where α is the geometrical factor, κ is the transmission coefficient, ν is the vibration frequency, and a_0 is the jump distance of a cation from the lattice site to the neighboring vacancy.

By comparing this relationship with empirical Eq. (7), the activation entropy (ΔS_m) and enthalpy (ΔH_m) of the diffusion can be calculated. From this comparison it follows directly that $\Delta H_m = 76.4$ kJ/mol. Assuming, in turn, α and $\kappa = 1$, $a_0 = 5.30$ Å (*1*), and calculating the vibration frequency of cations according to the relation (*19*)

$$\nu = (2/\pi a_0)(\Delta H_m/M)^{1/2} = 1.35 \times 10^{12}\ \mathrm{s}^{-1}, \qquad (9)$$

(where M is the atomic weight of manganese) one obtains by combining Eqs. (7) and (8), $\Delta S_m = 10.4$ J/mol deg.

Conclusions

The results obtained in the present work concerning the defect mobility in metal deficient manganous sulfide allow the following conclusions to be formulated:

1. The independence of chemical and defect diffusion coefficients with the departure from stoichiometry confirms the defect model of $Mn_{1-y}S$, according to which doubly ionized cation vacancies and electron holes (the dominant disorder in this compound) do not interact and are randomly distributed in the crystal lattice.

2. As the diffusion coefficient of defects is a measure of their mobility, it can be stated further that the diffusional transport of cations in $Mn_{1-y}S$ occurs by a simple vacancy mechanism, consisting in the jumping of Mn^{2+} ions from the lattice sites into the neighboring cation vacancies.

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