Thermodynamics and kinetics of point defects in manganous sulphide

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The defect equilibria and diffusion kinetics of point defects and manganese ions in manganese sulphide have been discussed with the background of available literature data. It has been shown that the behaviour of defects over the whole phase field of this compound can be satisfactorily described in terms of point defect thermodynamics. Over the major part of the homogeneity range, doubly ionized cation vacancies and electron holes are the dominating defects, manganous sulphide being a metal deficit p-type semiconductor ($Mn_{1-y}S$). Near the Mn/MnS phase boundary, on the other hand, doubly ionized interstitial cations and quasi-free electrons prevail, the sulphide being thus a metal excess n-type semiconductor ($Mn_{1+y}S$). The enthalpy and entropy of cation vacancy formation in $Mn_{1-y}S$ and those of interstitial cations in $Mn_{1+y}S$, have been calculated. Both near and at the stoichiometric composition, the defect structure of manganous sulphide is more complex and strongly dependent on temperature. Below about 1100 K, intrinsic Frenkel electronic disorder dominates. In agreement with the defect model it has been shown that the self-diffusion of cations in $Mn_{1-y}S$ proceeds by a simple vacancy mechanism via doubly ionized cation vacancies, randomly distributed in the crystal lattice. The activation enthalpy and entropy of this process have been calculated. On the other hand, diffusion of manganese ions in $Mn_{1+y}S$ proceeds by an interstitial mechanism, in which the cation enters from its normal lattice site into a neighbouring interstitial position. In agreement with theoretical predictions, the activation enthalpy of this process has been found to be considerably higher than that of the vacancy diffusion. It has been demonstrated that the minimum rate of manganese self-diffusion at a given temperature corresponds very well to the stoichiometric composition of the sulphide, which is again in agreement with the defect model.

1. Introduction

Manganous sulphide, α-MnS, having rock-salt structure, is the only stable compound in the Mn–S system above 473 K [1, 2]. In contrast to the other transition metal sulphides, this compound shows very small deviations from stoichiometry, and thereby defect concentrations are even smaller than those of manganous oxide, MnO [3]. This is illustrated in Fig. 1 showing the temperature dependence of the maximum non-stoichiometry for some metal sulphides and oxides. Thus, it may be assumed that the interaction between point defects in this compound is negligible and their behaviour at high temperatures can be treated in terms of statistical point defect thermodynamics. Consequently, the transport properties of this sulphide should also follow the rules of solid state diffusion theory based on point defect thermodynamics [4, 5].

The physico-chemical properties of manganous sulphide have been studied extensively by different authors [6–16] using various experimental techniques. In particular, non-stoichiometry [8, 14–16] and electrical conductivity [9–12] have been studied as a function of temperature and sulphur activity over the whole homogeneity range of this compound. Further,

the kinetics of manganese sulphidation was the subject of detailed systematic investigations [6–21]. Finally, the self-diffusion coefficient of manganese in α-MnS has also been measured or estimated [13–16, 19, 21] at different temperatures and sulphur pressures. The aim of the present paper is an attempt to summarize these results, and on this basis to quantitatively describe defect equilibria and diffusion kinetics of manganese ions in this interesting transition metal sulphide.

2. Defect equilibria in manganous sulphide

It has been shown [8, 9, 12] that in the major part of the phase field, corresponding to higher sulphur activities, α-MnS is a metal deficit p-type semiconductor with the predominant defects being cation vacancies and electron holes ($Mn_{1-y}S$). At very low sulphur activities, on the other hand, near and at the Mn/MnS phase boundary, this sulphide has been found to be a metal excess n-type semiconductor with interstitial cations and quasi-free electrons as predominant defects ($Mn_{1+y}S$). In the intermediate part of the phase field in turn, near and at the stoichiometric composition, the defect structure is strongly
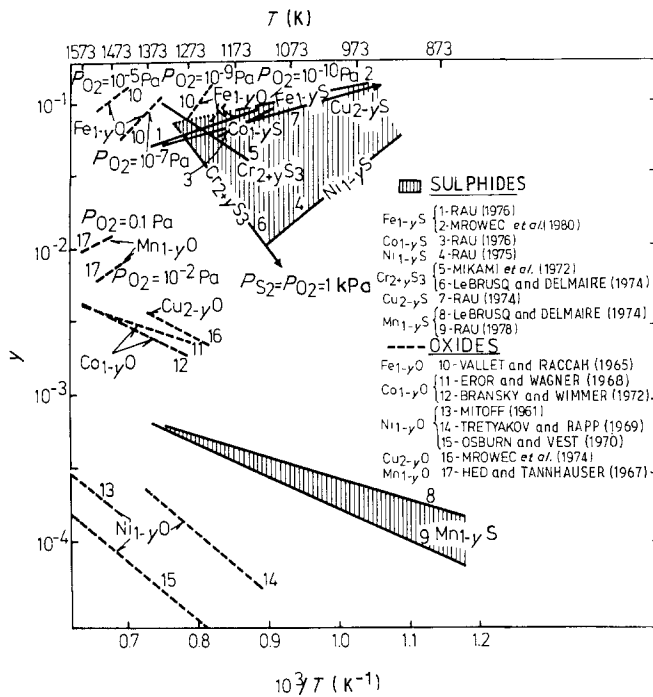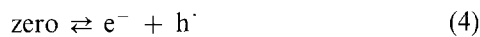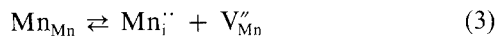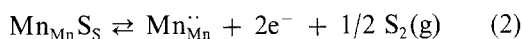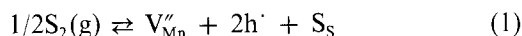
Figure 1 Maximum nonstoichiometry for some metal sulphides and oxides [3] plotted by dependence on $1/T$.

dependent on temperature. In the range of lower temperatures, intrinsic *ionic* disorders of the Frenkel-type prevail, electron holes and quasi-free electrons being minority defects [16]. At higher temperatures on the other hand, intrinsic *electronic* defects predominate, cation vacancies and interstitial cations being minority defects [16]. This gradual change of defect situations in manganous sulphide with temperature is illustrated in Fig. 2.

It has been shown [17] that the sulphide scale on manganese grows by the outward diffusion of cations without any participation of the inward diffusion of sulphur. It may then be assumed that the anion sub-lattice in manganous sulphide is perfectly ordered, the concentrations of anion vacancies or interstitial anions being negligibly small as compared to the degree of cation sublattice disorder. Thus, in agreement with the experimental data presented in Fig. 2, all important defect equilibria in $Mn_{1\pm y}S$ can be described by the following quasi-chemical equations:

$$1/2S_2(g) \rightleftarrows V''_{Mn} + 2h^{\cdot} + S_S \qquad (1)$$

$$Mn_{Mn}S_S \rightleftarrows Mn^{\cdot\cdot}_i + 2e^- + 1/2\,S_2(g) \qquad (2)$$

$$Mn_{Mn} \rightleftarrows Mn^{\cdot\cdot}_i + V''_{Mn} \qquad (3)$$

$$zero \rightleftarrows e^- + h^{\cdot} \qquad (4)$$

(The Kröger–Vink notation [22] of defects is used throughout this paper.) As the concentration of all types of defects in manganous sulphide is very low, their ideal behaviour may be assumed enabling the application of the mass action law to all defect equilibria. Using the available experimental data, the following expressions for the equilibrium constants, describing extrinsic and intrinsic disorder have been obtained:

$$K_V = [V''_{Mn}][h^{\cdot}]^2 p_{S_2}^{-1/2}$$

$$= 4.335 \times 10^{-4} \exp\left(-\frac{124.4\,kJ\,mol^{-1}}{RT}\right) \qquad (5)$$

$$K_i = [Mn^{\cdot\cdot}_i][e^-]^2 p_{S_2}^{1/2}$$

$$= 1.46 \times 10^{-1} \exp\left(-\frac{452\,kJ\,mol^{-1}}{RT}\right) \qquad (6)$$

$$K_F = [V''_{Mn}][Mn^{\cdot\cdot}_i]$$

$$= 3.93 \times 10^{-10} \exp\left(\frac{13.7\,kJ\,mol^{-1}}{RT}\right) \qquad (7)$$

$$K_e = [e^-][h^{\cdot}]$$

$$= 4.018 \times 10^2 \exp\left(\frac{281.4\,kJ\,mol^{-1}}{RT}\right) \qquad (8)$$

where K_V and K_i denote the equilibrium constants of extrinsic disorder in $Mn_{1-y}S$ and $Mn_{1+y}S$, respectively; K_F is the equilibrium constant of the formation of intrinsic ionic defects and K_e describes the intrinsic electronic disorder (square brackets denote defect concentrations expressed in mole fractions).

The intrinsic ionic and electronic defects are only temperature dependent (Equations 7 and 8). Extrinsic defects on the other hand, the formation of which results in non-stoichiometry, also depend on the sulphur pressure (Equations 5 and 6). Consequently, using appropriate electro-neutrality conditions ($[V''_{Mn}] = 1/2[h^{\cdot}]$ and $[Mn^{\cdot\cdot}_i] = 1/2[e^-]$), the equilibrium concentrations of these defects can be calculated as a function of temperature and sulphur pressure. For metal deficit ($Mn_{1-y}S$) and metal excess ($Mn_{1+y}S$) manganous sulphide, the following relationships have been obtained:

$$[V''] = (1/4K_V)^{1/3} p_{S_2}^{1/6}$$

$$= 4.77 \times 10^{-2} p_{S_2}^{1/6} \exp\left(-\frac{41.5\,kJ\,mol^{-1}}{RT}\right) \qquad (9)$$

$$[h^{\cdot}] = (2K_V)^{1/3} p_{S_2}^{1/6}$$

$$= 9.535 \times 10^{-2} p_{S_2}^{1/6} \exp\left(-\frac{41.5\,kJ\,mol^{-1}}{RT}\right) \qquad (10)$$
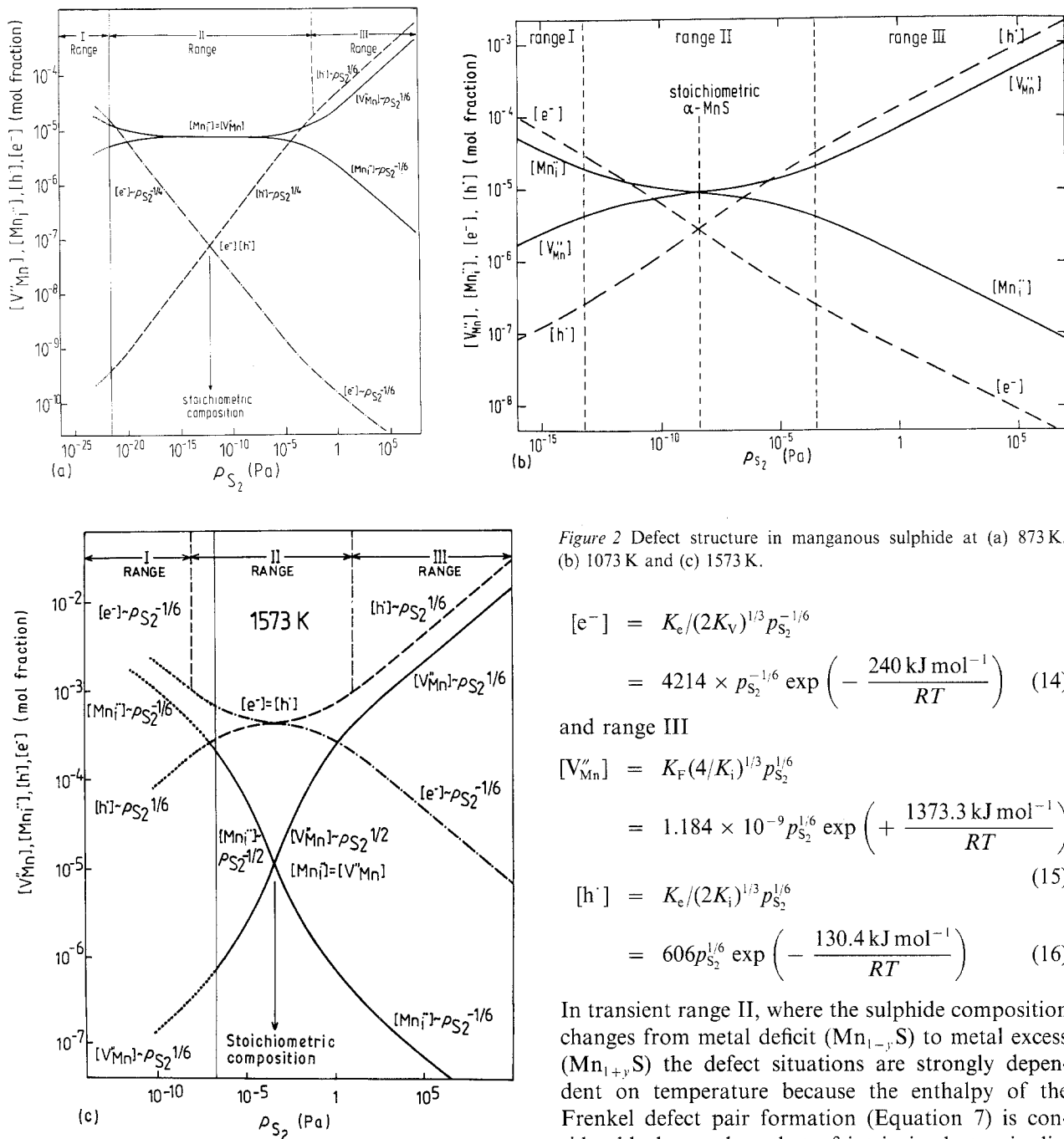
Figure 2 Defect structure in manganous sulphide at (a) 873 K, (b) 1073 K and (c) 1573 K.

$$[e^-] = K_e/(2K_V)^{1/3} p_{S_2}^{-1/6}$$

$$= 4214 \times p_{S_2}^{-1/6} \exp\left(-\frac{240\,\text{kJ mol}^{-1}}{RT}\right) \quad (14)$$

and range III

$$[V_{Mn}''] = K_F(4/K_i)^{1/3} p_{S_2}^{1/6}$$

$$= 1.184 \times 10^{-9} p_{S_2}^{1/6} \exp\left(+\frac{1373.3\,\text{kJ mol}^{-1}}{RT}\right)$$
$$\quad (15)$$

$$[h^{\cdot}] = K_e/(2K_i)^{1/3} p_{S_2}^{1/6}$$

$$= 606 p_{S_2}^{1/6} \exp\left(-\frac{130.4\,\text{kJ mol}^{-1}}{RT}\right) \quad (16)$$

In transient range II, where the sulphide composition changes from metal deficit ($Mn_{1-y}S$) to metal excess ($Mn_{1+y}S$) the defect situations are strongly dependent on temperature because the enthalpy of the Frenkel defect pair formation (Equation 7) is considerably lower than that of intrinsic electronic disorder (Equation 8). Consequently, at lower temperatures intrinsic ionic disorder prevails (Fig. 2) being independent of sulphur activity:

$$[V_{Mn}''] = [Mn_i^{\cdot\cdot}] = K_F^{1/2} \gg [h^{\cdot}] \text{ and } [e^-] \quad (17)$$

and at higher temperatures, intrinsic electronic defects predominate (see Fig. 4) being again pressure independent:

$$[h^{\cdot}] = [e^-] = K_e^{1/2} \gg [V_{Mn}''] \text{ and } [Mn_i^{\cdot\cdot}] \quad (18)$$

Using these relations and considering Equations 5 to 8, the concentrations of minority defects as a function of temperature and sulphur pressure, in the discussed intermediate range II, can be written as follows.

Case I. Intrinsic ionic disorder prevails (Equation 17):

$$[h^{\cdot}] = \left(\frac{K_V^{1/2}}{K_F^{1/4}}\right) p_{S_2}^{1/4}$$

$$= 4.68 p_{S_2}^{1/4} \exp\left(-\frac{58.8\,\text{kJ mol}^{-1}}{RT}\right) \quad (19)$$

$$[Mn_i^{\cdot\cdot}] = (1/4\,K_i)^{1/3} p_{S_2}^{-1/6} \exp\left(-\frac{151\,\text{kJ mol}^{-1}}{RT}\right)$$
$$\quad (11)$$

$$[e^-] = (2K_i)^{1/3} p_{S_2}^{-1/6}$$

$$= 0.0663 p_{S_2}^{-1/6} \exp\left(-\frac{151\,\text{kJ mol}^{-1}}{RT}\right) \quad (12)$$

As illustrated in Fig. 2, these four relationships describe the concentrations of ionic and electronic defects dominating in two limiting ranges of sulphur pressure I and III. The behaviour of minority defects in the same pressure intervals (Fig. 2) can be described by combining Equations 7 and 8 with Equations 9 to 12 giving

range I

$$[Mn_i^{\cdot\cdot}] = K_F(4K_V)^{1/3} p_{S_2}^{-1/6}$$

$$= 8.24 \times 10^{-9} p_{S_2}^{-1/6} \exp\left(+\frac{27.8\,\text{kJ mol}^{-1}}{RT}\right)$$
$$\quad (13)$$

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and

$$[e^-] = \left(\frac{K_i^{1/2}}{K_F^{1/4}}\right) p_{S_2}^{-1/4}$$

$$= 85.8 p_{S_2}^{-1/4} \exp\left(-\frac{223\,\text{kJ mol}^{-1}}{RT}\right) \quad (20)$$

Case II. Intrinsic electronic disorder prevails (Equation 18):

$$[V_{Mn}''] = (K_V/K_e) p_{S_2}^{1/2}$$

$$= 1.079 \times 10^{-6} p_{S_2}^{1/2} \exp\left(+\frac{157.0\,\text{kJ mol}^{-1}}{RT}\right) \quad (21)$$

and

$$[Mn_i^{\cdot\cdot}] = (K_i/K_e) p_{S_2}^{-1/2}$$

$$= 3.63 \times 10^{-4} p_{S_2}^{-1/2} \exp\left(-\frac{171.0\,\text{kJ mol}^{-1}}{RT}\right) \quad (22)$$

From Equations 5 to 8 it follows that at equilibrium sulphur pressure manganous sulphide has the stoichiometric composition

$$p_{S_2}(\text{stoich.}) = K_i/K_V$$

$$= 337 \exp\left(-\frac{327.6\,\text{kJ mol}^{-1}}{RT}\right) \quad (23)$$

These pressures are marked on the defect structure diagrams presented in Fig. 2.

Summing up the above considerations concerning the defect situations in manganous sulphide, the enthalpy and entropy of point defect formation can be calculated. This can readily be done by comparing empirical Equations 9 and 11 with theoretical relationships resulting from point defect thermodynamics [4, 5]. From Equations 9 and 11 it is evident that the concentrations of doubly ionized cation vacancies in $Mn_{1-y}S$ and doubly ionized interstitial cations in $Mn_{1+y}S$ are given by the following functions of temperature and equilibrium sulphur pressure:

$$[V_{Mn}''] = 0.63 p_{S_2}^{1/6} \exp\left(\frac{1/3\Delta S_f^V}{R}\right)$$

$$\times \exp\left(-\frac{1/3\Delta H_f^V}{RT}\right) \quad (24)$$

and

$$[Mn_i^{\cdot\cdot}] = 0.63 p_{S_2}^{-1/6} \exp\left(\frac{1/3\Delta S_f^i}{R}\right)$$

$$\times \exp\left(-\frac{1/3\Delta H_f^i}{RT}\right) \quad (25)$$

where ΔH_f^V, ΔH_f^i, and ΔS_f^V, ΔS_f^i denote the enthalpies and entropies of formation of cation vacancies and interstitial cations, respectively. Comparing Equations 9 and 24, as well as Equations 11 and 25, the following values for enthalpy and entropy of defect formation have been obtained: $\Delta H_f^V = 124\,\text{kJ mol}^{-1}$; $\Delta H_f^i = 452\,\text{kJ mol}^{-1}$; $\Delta S_f^V = -64.4\,\text{J mol}^{-1}\,\text{deg}^{-1}$; $\Delta S_f^i = -16.0\,\text{J mol}^{-1}\,\text{deg}^{-1}$.

3. Diffusion kinetics in manganous sulphide

From the defect structure model described above, it follows clearly that the mechanism and kinetics of cation diffusion in manganous sulphide should strongly depend upon the thermodynamic conditions. In particular, with decreasing sulphur activity this mechanism should change near the stoichiometric composition of the sulphide, from vacancy to interstitial diffusion. Also, the dependence of the diffusion rate on temperature and sulphur pressure should be different in ranges I and III (Fig. 2). In order to prove this conclusion, the self-diffusion coefficient of manganese must be known as a function of temperature and sulphur pressure over the whole homogeneity range of the MnS phase. Because of considerable experimental difficulties encountered in studying high temperature processes under a sulphur atmosphere, this important problem has not been solved so far. In fact, no direct experimental results are available concerning the self-diffusion rate of manganese in manganous sulphide. However, the kinetics of manganese sulphidation has been extensively studied as a function of temperature and sulphur activity [16–21], as well as the evaporation rate of the metal from the surface of an MnS scale formed on manganese [13–16]. All these results make it possible to calculate the self-diffusion coefficient of cations in the discussed sulphide as a function of temperature and sulphur pressure, and to derive several conclusions concerning the kinetics and thermodynamics of point defect diffusion in this material.

3.1. Self-diffusion of manganese in metal deficit manganous sulphide

It has been shown in the previous section that the major part of the phase field predominant defects in manganous sulphide are doubly ionized cation vacancies ($Mn_{1-y}S$). The sulphide scale on manganese grows by the outward diffusion of cations, and the overall reaction rate is diffusion controlled as indicated by the parabolic course of the sulphidation process [16–21]. Sulphidation studies have been carried out as a function of temperature (873–1373 K) and sulphur pressure (10^{-6}–10^{-5} Pa) at strictly defined thermodynamic conditions, and the kinetic results can be summarized by the following empirical equation:

$$k_p = 7.23 \times 10^{-3} p_{S_2}^{1/6} \exp\left(-\frac{120\,\text{kJ mol}^{-1}}{RT}\right) \quad (26)$$

where k_p is the parabolic rate constant of sulphidation, expressed in ($\text{cm}^2\,\text{sec}^{-1}$) according to the familiar Tammanns's parabolic rate law:

$$\frac{dx}{dt} = \frac{k_p}{x} \quad (27)$$

where x is the thickness of the scale at time t.

These results have been obtained at sulphur pressures exceeding, even at the lowest pressure, the dissociation pressure of manganous sulphide by several orders of magnitude. Therefore, the parabolic rate constants of manganese sulphidation can be utilized for the calculation of self-diffusion coefficients

of Mn in $Mn_{1-y}S$ on the basis of Wagner's theory of metal oxidation [23]:

$$k_p = \int_{p'_{S_2}}^{p''_{S_2}} D_{Mn}\, d(\ln p_{S_2}) \qquad (28)$$

where p'_{S_2} and p''_{S_2} denote the sulphur pressures at the metal/scale and scale/gas interface, respectively. To integrate Equation 28, it is necessary to express D_{Mn} as a function of p_{S_2}. This functional relationship will depend upon the defect structure of the sulphide. Based on the defect model described above, it is possible to assume that under the discussed experimental conditions, the predominant defects over the most part of the cross-section of the sulphide scale growing on manganese are doubly ionized cation vacancies. It may be further assumed that because of low deviations from stoichiometry ($y < 0.01$) and thereby low defect concentrations, the mobility of cation vacancies is independent of their concentration, and consequently, that the self-diffusion coefficient of cations $Mn_{1-y}S$, D_{Mn}^v, is directly proportional to the concentration of defects. Then, considering Equation 9, one obtains [4, 5]:

$$D_{Mn}^v = D_V[V_{Mn}''] = D_{Mn}^0 p_{S_2}^{1/6} \qquad (29)$$

where D_V denotes the vacancy diffusion coefficient, and D_{Mn}^0 the self-diffusion coefficient of Mn in $Mn_{1-y}S$ at $p_{S_2} = 1$ atm. From the comparison of this relationship with the empirical Equation 26 it follows that the pressure dependence of k_p and D_{Mn} is the same, clearly indicating that the assumption was correct concerning the type of predominant defects and their mobility in the sulphide scale growing on manganese.

Introducing Equation 29 into Equation 28 and considering the case $p''_{S_2} \gg p'_{S_2}$, integration of Equation 28 results, after further transformations, in the following simple relationship:

$$k_p = 3D_{Mn}^v \qquad (30)$$

However, the self-diffusion coefficient of Mn in $Mn_{1-y}S$ can be calculated also without any assumption concerning its dependence on sulphur pressure. Differentiating Equation 28 with respect to p''_{S_2} one arrives at the following relationship:

$$D_{Mn}^v = \left(\frac{dk_p}{d(\ln p''_{S_2})}\right)_{p'_{S_2}} \qquad (31)$$

Such procedure, in the literature called Fueki–Wagner method [24–26], only needs the determination of the pressure dependence of the parabolic rate constant of metal oxidation. This has been done in the case of manganese sulphidation (Equation 26). Thus, the self-diffusion coefficient of manganese in $Mn_{1-y}S$ has been calculated as a function of temperature and sulphur pressure using both methods (Equations 30 and 31). The results of these calculations are presented in Figs 3 and 4, in double logarithmic and Arrhenius plots, respectively. From Fig. 3 it follows clearly that both methods of calculation lead to the same results, which implies that as predicted, the mobility of cation vacancies in $Mn_{1-y}S$ does not depend upon their concentration. It can also be seen that the pressure dependence of D_{Mn}^v is satisfactorily described by
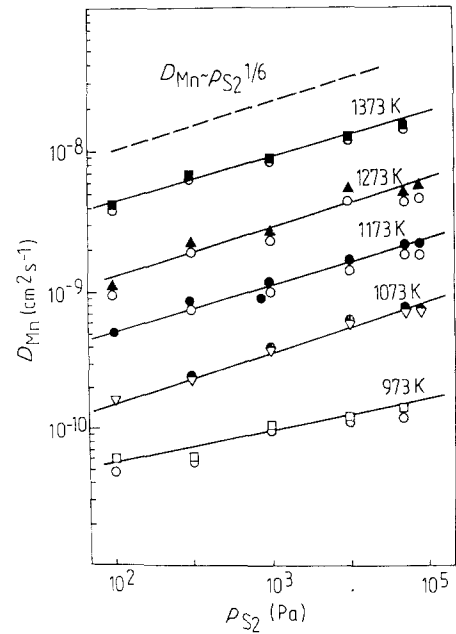

Figure 3 Dependence of the self-diffusion coefficient of manganese in manganous sulphide on sulphur pressure for several temperatures, values calculated with Equations 30 and 31, respectively.

Equation 29 and its temperature dependence follows the Arrhenius relationship (Fig. 4). Thus, the dependence of the self-diffusion coefficient of cations in $Mn_{1-y}S$ on temperature and sulphur pressure can be described by the following empirical equation:

$$D_{Mn}^v = 6.7 \times 10^{-4} p_{S_2}^{1/6} \exp\left(-\frac{121\,\text{kJ mol}^{-1}}{RT}\right) \qquad (32)$$

From the comparison of Equations 32 and 9 it follows that as assumed, the self-diffusion coefficient of Mn in $Mn_{1-y}S$ is directly proportional to the concentration of cation vacancies $[V_{Mn}'']$ and consequently, their diffusion coefficient D_V is independent of $[V_{Mn}'']$. As the defect diffusion coefficient is a direct measure of their mobility, it can be stated that the diffusional transport of cations in $Mn_{1-y}S$ occurs by a simple vacancy
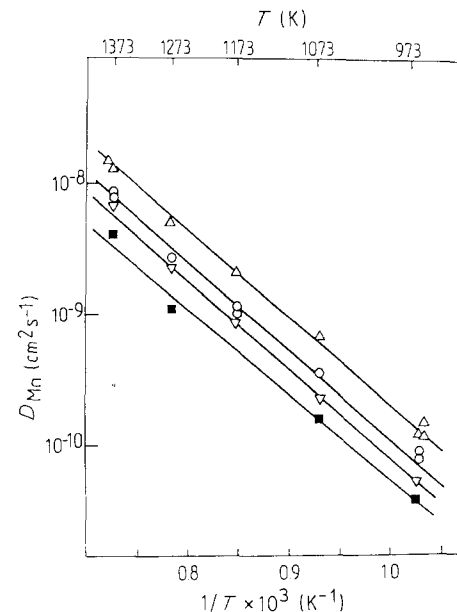

Figure 4 Temperature dependence of the self-diffusion coefficient of manganese in magnanous sulphide at different sulphur pressures. (△) 5×10^4 Pa, (○) 10^3 Pa, (▽) 10^2 Pa, (■) 10 Pa.

mechanism via non-interacting completely ionized cation vacancies, being randomly distributed in the crystal lattice.

The results described above enable the activation enthalpy and entropy of the discussed vacancy diffusion in $Mn_{1-y}S$ to be calculated. Introducing Equations 32 and 9 into Equation 29 yields:

$$D_V = 1.41 \times 10^{-2} \exp\left(-\frac{79.7\,\mathrm{kJ\,mol^{-1}}}{RT}\right) \quad (33)$$

From this empirical equation, the activation enthalpy ΔH_m^v, and the activation entropy, ΔS_m^v, of vacancy diffusion can be obtained by comparing the following theoretical equation [4, 5]:

$$D_V = \alpha a_0^2 \kappa v \exp\left(\frac{\Delta S_m^v}{R}\right) \exp\left(-\frac{\Delta H_m^v}{RT}\right) \quad (34)$$

where α is the geometrical factor, κ the transmission coefficient, v the vibration frequency and a_0^2 the jump distance. From a comparison of Equations 33 and 34 it follows that $\Delta H_m^v = 79.7\,\mathrm{kJ\,mol^{-1}}$. Assuming in turn α and $\kappa = 1$ and $a_0 = 0.530\,\mathrm{nm}$ [27], as well as calculating the vibration frequency of cations according to relation [28]:

$$v = (2/\pi a_0)(\Delta H_m^v/M)^{1/2} = 1.35 \times 10^{12}\,\mathrm{sec^{-1}} \quad (35)$$

(where M is the atomic mass of Mn) one obtains by combining Equations 33 and 34, $\Delta S_m^v = 11\,\mathrm{J\,mol^{-1}\,deg^{-1}}$.

3.2. Self-diffusion of manganese in metal excess manganous sulphide

In the very narrow part of the phase field close to the Mn/MnS phase boundary, manganous sulphide is a metal excess n-type semiconductor $(Mn_{1+y}S)$ with doubly ionized interstitial cations and quasi-free electrons as predominant defects (see Fig. 2). Under these conditions (very low sulphur pressures), self-diffusion coefficients of Mn in $Mn_{1+y}S$ cannot be obtained from the manganese sulphidation kinetics. However, they can be calculated from the evaporation rate of manganese from the surface of a MnS-scale layer, performed on Mn using a method developed by Kofstad [29]. This method, the so-called diffusion–evaporation method, involves oxidation (or sulphidation) of a given metal to form a dense, single layer scale of the lowest valent oxide (or sulphide), i.e. the compound which is in equilibrium with the metallic phase. The specimen is then treated in high vacuum. As no oxidation (or sulphidation) takes place, metal ions and electrons diffuse outward through the scale and metal atoms continuously evaporate from the scale surface, as depicted in Fig. 5. If the evaporation of the metal is governed by its diffusion through the scale, the self-diffusion coefficient of cations in the compound forming the scale can be calculated from the evaporation rate measurements. This rate can be determined thermogravimetrically by measuring the mass loss of the specimen as a function of time.

Several requirements must be met in order to use this method. The vapour pressure of the compound forming the scale must be sufficiently low at experimental conditions so that no oxide (or sulphide) is lost
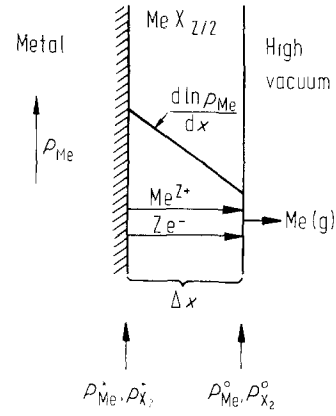

Figure 5 Schematic representation of the diffusion–evaporation in oxides or sulphides during high vacuum treatment of pre-oxidized (or pre-sulphidized) metal specimens [29], for studies of metal self-diffusion in equilibrium with metal [29].

by evaporation from the specimen during the high vacuum treatment. The oxidant activity in the outer surface of the scale must be sufficiently low so that virtually no oxidant is lost from the scale by its decomposition. The vapour pressure of the metal at the outer scale surface must be several orders of magnitude higher than that of the oxidant so that only metal atoms evaporate. The partial pressure of the metal at the metal/scale interface, p_M^*, must be many orders of magnitude higher than the partial pressure of oxidant at the same interface, i.e. $p_M^* \gg p_{X_2}^*$.

These requirements limit the applicability of the method to oxides or sulphides with high thermodynamic stability. Kofstad [29, 30] has shown that the Mn/MnO system represents a favourable example and has been able to successfully apply this method for the determination of the self-diffusion coefficient of manganese in manganous oxide in equilibrium with the metallic phase.

It is easy to demonstrate that the Mn/MnS system is also suitable for this kind of measurement. For instance, at 1373 K $p_{Mn}^*/p_{S_2}^* = 6 \times 10^{10}$, and the evaporation and decomposition rates of MnS are many orders of magnitude lower than the evaporation rate of manganese metal [31–33]. Thus, during isothermal annealing of a manganese specimen covered with a dense manganous sulphide layer in high vacuum, the metal ions and electrons will diffuse outward through the scale with constant thickness and manganous atoms will evaporate from the surface of the specimen at a constant rate.

The flux of the Mn-atoms through a scale with thickness Δx is given by the following relationship [29]:

$$j_{Mn} = -\left(c_{Mn} \int_{p_{Mn}^*}^{p_{Mn}^0} D_{Mn}\, \mathrm{d}(\ln p_{Mn})\right) \Delta x^{-1} \quad (36)$$

where p_{Mn}^* and p_{Mn}^0 denote the partial pressures of manganese vapour at the inner and outer scale surface, respectively (see Fig. 5), and c_{Mn} is the concentration of Mn atoms in α-MnS. To integrate Equation 36, it is necessary to express D_{Mn} as a function of p_{Mn}. This relationship depends upon the defect structure of the sulphide. As the predominant defects in manganous sulphide in equilibrium with the metal are doubly

ionized interstitial cations, the dependence of their concentration on sulphur pressure is described by Equation 11. In this relationship the sulphur pressure can be substituted by the corresponding pressure of Mn vapour using the equation:

$$K_{eq} = p_{S_2}^{1/2} p_{Mn} \tag{37}$$

describing the equilibrium of the reaction:

$$MnS(s) \rightleftharpoons 1/2 S_2(g) + Mn(g) \tag{38}$$
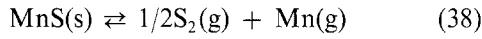
Introducing Equation 37 into Equation 11 gives:

$$[Mn_i^{\cdot\cdot}] = (K_i/4K_{eq})^{1/3} p_{Mn}^{1/3} \tag{39}$$

As the self-diffusion coefficient of manganese ions in $Mn_{1+y}S$, D_{Mn}^i, is given by [4, 5]:

$$D_{Mn}^i = D_i [Mn_i^{\cdot\cdot}] \tag{40}$$

(where D_i is the diffusion coefficient of interstitial defects), introducing Equation 40 into Equation 39 yields:

$$D_{Mn}^i = (K_i/4K_{eq})^{1/3} = D_i p_{Mn}^{1/3} = D_{Mn}^+ p_{Mn}^{1/3} \tag{41}$$

where D_{Mn}^+ denotes the self-diffusion coefficient of manganese in $Mn_{1+y}S$ at $p_{Mn} = 1$ atm. By introducing this relation into Equation 36 and integrating over the thickness Δx and between p_{Mn}^0 and p_{Mn}^*, the flux of Mn atoms is given by:

$$j_{Mn} = 3c_{Mn} D_{Mn}^+ [(p_{Mn}^*)^{1/3} - (p_{Mn}^0)^{1/3}] \frac{1}{\Delta x} \tag{42}$$

Considering Equation 41 and the fact that $p_{Mn}^* \gg p_{Mn}^0$, Equation 42 assumes the following final form:

$$j_{Mn} = 3c_{Mn} D_{Mn}^* (\Delta x)^{-1} \tag{43}$$

where D_{Mn}^* is the self-diffusion coefficient of manganese in $Mn_{1+y}S$ in equilibrium with the metallic phase.

From Equation 43 it follows that under these conditions, the self-diffusion coefficient of Mn in the $Mn_{1+y}S$ scale is independent of its thickness and the flux of Mn atoms is the following function of this parameter:

$$j_{Mn} = \text{const.}(\Delta x)^{-1} \tag{44}$$

On the other hand, if one assumes that the predominant defects in the sulphide in equilibrium with the metallic phase are doubly ionized cation vacancies and electron holes, then going through the same procedure as for the previously discussed case, it can be shown that the expression for the flux of Mn atoms through the scale is given by:

$$j_{Mn} = 3c_{Mn} D_{Mn}^0 (\Delta x)^{-1} \tag{45}$$

where D_{Mn}^0 denotes the self-diffusion coefficient of manganese in the scale at its outer surface. In this case, the self-diffusion coefficient of manganese in the scale depends upon its thickness and it can be shown that the flux of Mn atoms is given by [29]:

$$j_{Mn} = \text{const.}(\Delta x)^{-3/4} \tag{46}$$

From a comparison of Equations 44 and 46 it follows, from studying the diffusional evaporation rate of manganese as a function of the scale thickness, that not only the diffusion coefficient of cations in manga-
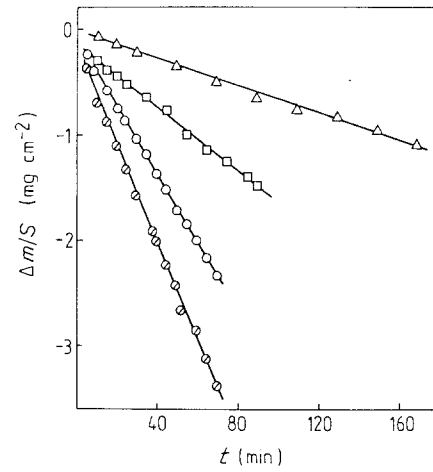

Figure 6 Diffusion–evaporation runs for the Mn/MnS/vacuum system at 1273 K for scales of different thickness [14, 15]. (○) 48 μm, (◇) 108 μm, (□) 116 μm, (△) 240 μm.

nous sulphide can be determined but also important information concerning the type of predominant defects in this compound in equilibrium with the metallic phase is obtained.

The diffusion-controlled evaporation of manganese has been determined as a function of temperature (1073–1373 K) and the scale thickness (48–240 μm) using a special micro-thermobalance [34], enabling the determination of mass changes of a given specimen as a function of time in strictly defined thermodynamic conditions, with the sensitivity of $\pm 3 \times 10^{-6}$ g. The experimental procedure and the results of evaporation kinetics have been described elsewhere [13–15]. For illustration, Fig. 6 shows typical runs obtained at 1273 K for scales with different thickness. As can be seen, the evaporation of manganese from the surface of an α-MnS scale of a given thickness, preformed on Mn specimen, proceeds with a constant rate that is the smaller the thicker the scale. This indicates that all requirements are met in order to use this method for determination of the self-diffusion coefficient of manganese in manganous sulphide in equilibrium with the metal.

In Fig. 7 the flux of manganese ion diffusion through the scale is plotted as a function of its thickness for several temperatures. As can be seen, the rate of diffusion is inversely proportional to the scale
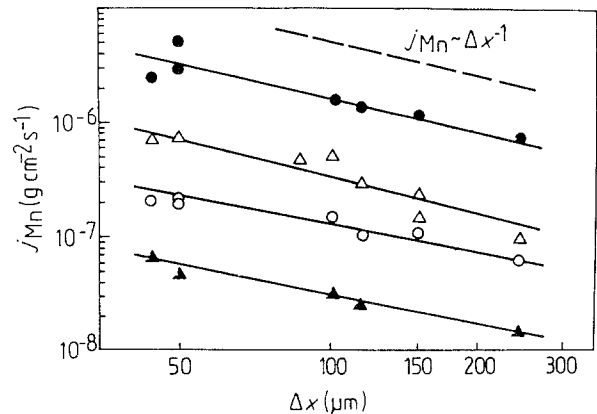

Figure 7 Dependence of manganese flux through the MnS-scale on its thickness as a double logarithmic plot at (●) 1373 K, (△) 1273 K, (○) 1173 K and (▲) 1073 K.
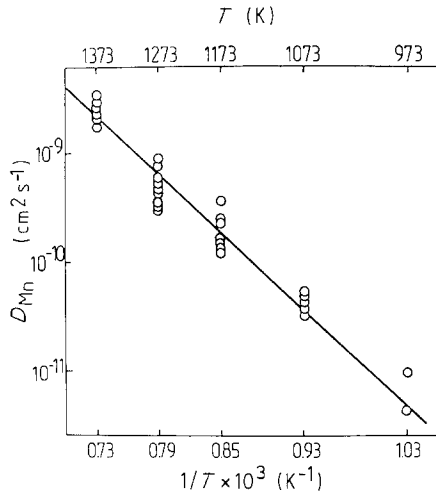
Figure 8 Temperature dependence of the self-diffusion coefficient of manganese in manganous sulphide, in equilibrium with the metallic phase.
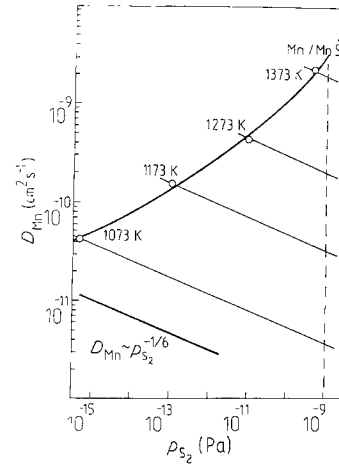

Figure 9 Dependence of the self-diffusion coefficient of manganese in manganous sulphide on the sulphur pressure for several temperatures.

thickness, clearly indicating that the condition given by Equation 44 is fulfilled. This conclusion is in agreement with the assumption resulting from the defect model that the diffusion of manganese in the sulphide in equilibrium with the metal proceeds by means of interstitial defects. Thus, Equation 43 was used to calculate the self-diffusion coefficient of cations in $Mn_{1+y}S$ as in the Arrhenius plot (Fig. 8). The linear character of this plot enables the temperature dependence of D_{Mn}^{*} to be described by the following empirical equation:

$$D_{Mn}^{*} = 1.89 \times 10^{-3} \exp\left(-\frac{158\,kJ\,mol^{-1}}{RT}\right) \quad (47)$$

However, the empirically determined activation energy of diffusion, $E_D = 158\,kJ\,mol^{-1}$, cannot be used for calculation of the activation enthalpy and entropy of the elementary acts of diffusion of interstitial cations in the crystal lattice of $Mn_{1+y}S$. To make such calculations, it is necessary to determine the activation energy of diffusion at constant sulphur activity [4, 5, 22]. The dependence described by Equation 47 does not fulfill this requirement because the self-diffusion coefficients determined at different temperatures, are related to different sulphur pressures, equal to the dissociation pressure of the sulphide. Nevertheless, these results can be utilized for the estimation of the activity energy of diffusion at a constant sulphur pressure. It has been shown that near the Mn/MnS phase boundary, the concentration of doubly ionized interstitial manganese ions in $Mn_{1+y}S$ decreases with increasing sulphur pressure according to Equation 11. As the concentration of these defects is very low, it is reasonable to assume that the mobility of interstitial cations in $Mn_{1+y}S$, as that of cation vacancies in $Mn_{1-y}S$, is independent of their concentration. Thus, considering Equations 11 and 40 one arrives at the conclusion that at a given temperature D_{Mn}^{i} in Mn_{1+y} should decrease with increasing sulphur pressure according to the equation:

$$D_{Mn}^{i} = const.(p_{S_2})^{-1/6} \quad (48)$$

It is then possible to construct the pressure depend-

ence of the self-diffusion coefficient of manganese in metal excess n-type manganous sulphide using D_{Mn}^{*} values determined at different temperatures by drawing straight lines in a double logarithmic plot with the slope $-1/6$. This diagram is presented in Fig. 9. From this plot it is possible to choose appropriate D_{Mn}^{i}-values corresponding to constant sulphur pressures at different temperatures as indicated by the vertical dotted line. The results of these calculations are presented in Fig. 10 as an Arrhenius plot. A straight line is obtained which made it possible to calculate the activation energy of manganese self-diffusion for constant sulphur pressure, and to express this dependency by the following empirical equation:

$$D_{Mn}^{i} = 0.252\,p_{S_2}^{-1/6} \exp\left(-\frac{269\,kJ\,mol^{-1}}{RT}\right) \quad (49)$$

It follows from this expression that the real value of the activation energy of manganese self-diffusion in $Mn_{1+y}S$ (E_D^{i}) is much higher than that (E_D^{v}) of Mn in $Mn_{1-y}S$ (Equation 32).
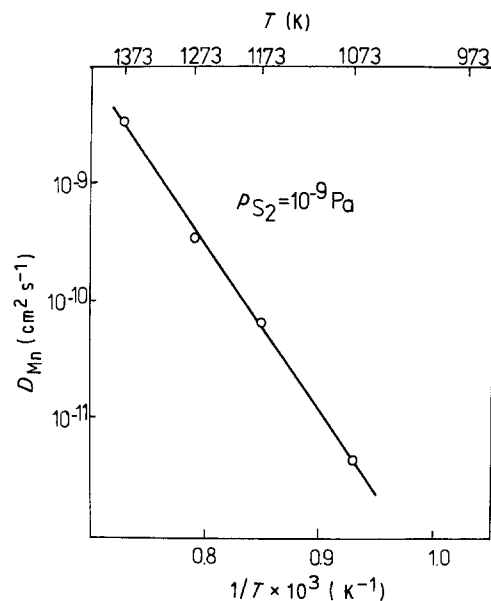

Figure 10 Temperature dependence of the self-diffusion coefficient of manganese in manganous sulphide at constant sulphur pressure.

Before discussing this problem, the activation enthalpy (ΔH_m^i) and entropy (ΔS_m^i) for diffusion of interstitial cations in $Mn_{1+y}S$ can be calculated. Introducing Equations 49 and 11 into Equation 40 gives:

$$D_i = 0.759 \exp\left(-\frac{118\,\mathrm{kJ\,mol^{-1}}}{RT}\right) \quad (50)$$

By comparing this empirical relationship with the theoretical Equation 34 which is valid for any mechanism of diffusion, one obtains:

$$\Delta H_m^i = 118\,\mathrm{kJ\,mol^{-1}} \text{ and } \Delta S_m^i$$
$$= 8.2\,\mathrm{J\,mol^{-1}\,deg^{-1}}$$

From a comparison of the empirical Equations 33 and 50 it follows that not only the activation energy but also the activation enthalpy of diffusion for interstitial cations in $Mn_{1+y}S$ is higher than that for cation vacancies in $Mn_{1-y}S$. This becomes conceivable if one considers possible diffusion mechanisms of interstitial cations in $Mn_{1+y}S$. In principle, there are two such possibilities [4, 5, 35, 36]. In the case of the body centred cubic lattice of α-MnS, the simple interstitial diffusion mechanism, consisting of successive jumps of Mn^{2+} ions from one interstitial position to another, can be excluded from purely geometrical reasons. It may be assumed that the diffusional transport of cations in metal excess manganous sulphide proceeds by an interstitial mechanism. This process, consisting of pushing the cation from its normal lattice site into a neighbouring interstitial position, needs more energy than the jump of a cation from the lattice site into a neighbouring vacancy, as a result of which $\Delta H_m^i > \Delta H_m^v$. As in addition, the enthalpy of formation of interstitial cations in $Mn_{1+y}S$ (Equation 11) is higher than that of cation vacancy formation in $Mn_{1-y}S$ (Equation 9), it becomes obvious that the activation energy of cation diffusion in $Mn_{1+y}S$ is considerably higher than that in $Mn_{1-y}S$.

4. Concluding remarks

Theoretical analysis of available experimental data concerning defect and transport properties of manganous sulphide indicates that in spite of the rather small homogeneity range the defect structure in this compound cannot be described by a simple model involving one type of predominant defect. In fact, in the major part of the phase field cation vacancies and electron holes are the predominant defects ($Mn_{1-y}S$), and near the Mn/MnS phase boundary, interstitial cations and quasi-free electrons prevail ($Mn_{1+y}S$). In the intermediate part of the phase field which is the larger the lower the temperature (see Fig. 2), the defect structure of manganous sulphide is much more complex. At lower temperatures ($<1100\,\mathrm{K}$), intrinsic ionic defects of the Frenkel-type predominate and at higher temperatures ($>1100\,\mathrm{K}$) intrinsic electronic disorder prevails. Consequently, the concentrations of ionic and electronic defects are not simple power functions of the equilibrium sulphur pressure over the whole homogeneity range of the sulphide and pass through minima at its stoichiometric composition (Fig. 2).
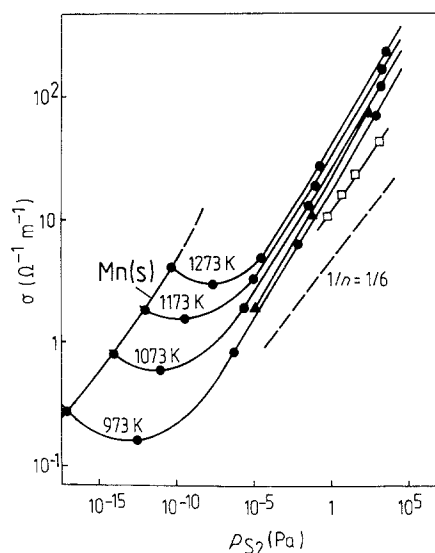

Figure 11 Dependence of the electrical conductivity of manganous sulphide on sulphur pressure at several temperatures. (●) From Rasner and Dherbomez (1981), (▲) from de Brusq et al. (1974) at 973 K, (□) from Fueki et al. (1970) at 1111 K.

This type of order is reflected in semiconducting and transport properties of the discussed sulphide, as illustrated in Figs 11 and 12. As can be seen, both the electrical conductivity (σ_{el}) and the self-diffusion coefficient of manganese depend in a similar way on the sulphur pressure, showing minimum values which in the case of diffusion correspond very well with the stoichiometric composition of the sulphide. The minima of electrical conductivity against sulphur pressure curves have been found at lower pressures than those observed on the self-diffusion curves. This may result either from experimental errors in determining the electrical conductivity at very low sulphur pressures, or from different mobilities of electron holes and quasi-free electrons.

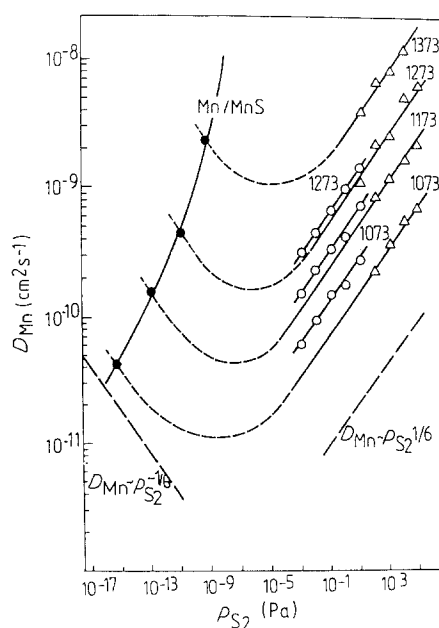The sulphur pressures $(p_{S_2}(\text{stoich.}))$ at which

Figure 12 Dependence of the self-diffusion coefficient of manganese in manganous sulphide on the sulphur pressure for several temperatures. (○) From Elrefaie and Smeltzer (1981), (●) and (△) this work.

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TABLE I Calculated sulphur pressures (Pa) at which manganous sulphide reaches stoichiometric composition (p_{S_2}(stoich)), and D_{Mn} and σ_{el} curves pass through the minimum

Temperature (K)	p_{S_2}(stoich.)	$p_{S_2}(D_{Mn}(min))$	$p_{S_2}(\sigma_{el}(min))$
873	8.4×10^{-13}	—	—
973	8.7×10^{-11}	—	1×10^{-12}
1073	3.8×10^{-9}	5.0×10^{-9}	1×10^{-11}
1173	8.7×10^{-8}	6.5×10^{-8}	1×10^{-9}
1273	1.2×10^{-6}	0.9×10^{-6}	1×10^{-8}
1373	1.2×10^{-5}	1.4×10^{-5}	—

manganous sulphide has the stoichiometric composition at a given temperature together with those corresponding to minimum values of Mn diffusion rate (D_{Mn}(min)) and electrical conductivity (σ_{el}(min)) are collected in Table I. It follows clearly from this comparison that there is excellent agreement between the minimum concentrations of ionic defects and lowest diffusion rates of cations in manganous sulphide.

As far as the mechanism of manganese diffusion is concerned, it should be noted that over the major part of the MnS-phase field this process proceeds by the simple vacancy mechanism consisting of Mn^{2+} ions jumping from the lattice sites into neighbouring cation vacancies. The activation enthalpy of this process is considerably smaller than that of interstitial diffusion of Mn^{2+} ions in the sulphide at or near equilibrium with the metallic phase. As the enthalpy of interstitial cation formation is also higher than that of cation vacancy formation (Equations 11 and 9), the activation energy of manganese diffusion in $Mn_{1+y}S$ is much higher than that in $Mn_{1-y}S$.

Calculated values of the thermodynamic parameters of vacancy and interstitial diffusion of manganese in manganous sulphide are collected in Table II. Analogous data for defect formation and activation energies of manganese diffusion are included. For comparison, corresponding data for nickel oxide and manganous oxide are also given. It is interesting to note that the activation enthalpies of vacancy diffusion in $Ni_{1-y}O$ and $Mn_{1-y}S$ as well as those of interstitial diffusion in $Mn_{1+y}O$ and $Mn_{1+y}S$ are very similar. In contrast, the enthalpies of defect formation are different, therefore, the activation energy of cation diffusion in $Mn_{1-y}S$ is lower than in $Ni_{1-y}O$ and that in $Mn_{1+y}S$ is lower than in $Mn_{1+y}O$.

Acknowledgements

TABLE II Thermodynamic parameters of the formation and migration of point defects in manganous sulphide, manganous oxide and nickel oxide

Compound	ΔH_f (kJ mol^{-1})	ΔS_f (J mol^{-1} deg^{-1})	ΔH_m (kJ mol^{-1})	ΔS_m (J mol^{-1} deg^{-1})	E_D (kJ mol^{-1})	References
$Mn_{1-y}S$	124	−64	80	11	121	This work
$Mn_{1+y}S$	452	−16	118	8.2	269	This work
$Mn_{1+y}O$	660	—	120	—	340	[30]
$Ni_{1-y}O$	441	−59	96	7.0	243	[37]

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