PHYSICAL REVIEW B VOLUME 56, NUMBER 14 1 OCTOBER 1997-II

Self-diffusion of manganese in nonstoichiometric manganous sulphide

J. Gilewicz-Wolter
University of Mining and Metallurgy, Faculty of Nuclear Physics and Techniques, al. Mickiewicza 30, 30-059 Cracow, Poland

M. Danielewski and S. Mrowec
University of Mining and Metallurgy, Department of Physical Chemistry of Solids, al. Mickiewicza 30, 30-059 Cracow, Poland

(Received 10 March 1997)

Self-diffusion of manganese in nonstoichiometric manganous sulphide, $Mn_{1\pm y}S$, has been studied as a function of temperature (1073–1373) K and sulfur activity (10^{-11}–10^{3}) Pa using radioactive ^{54}Mn isotope as a tracer. In agreement with the defect model of $Mn_{1\pm y}S$ it has been shown that at very low sulfur pressures, close to the Mn/MnS phase boundary, self-diffusion of cations in metal excess $Mn_{1+y}S$ proceeds by an interstitial mechanism, consisting of pushing a cation from its normal lattice site into neighboring interstitial position. At higher sulfur activities, on the other hand, cation self-diffusion in metal-deficit $Me_{1-y}S$ proceeds by a simple vacancy mechanism, consisting of Mn^{2+} ions jumping from the lattice sites into neighboring vacancies. It has been demonstrated that not only the temperature and pressure dependence of cation self-diffusion in metal-excess and metal-deficit manganous sulphide, but also absolute values of self-diffusion coefficients of this process are in excellent agreement with those calculated from manganese sulfidation and evaporation kinetics. This agreement clearly indicates that both these methods can successfully be utilized in studying the transport properties of transition-metal sulfides and oxides. [S0163-1829(97)07237-8]

INTRODUCTION

Physicochemical properties of manganous sulphide have been extensively studied by different authors using various experimental techniques. In particular, nonstoichiometry[1,2] and electrical conductivity[3–6] were investigated as a function of temperature and sulfur activity over the whole homogeneity range of this compound. Further, the kinetics and mechanism of manganese sulfidation was the subject of detailed investigations[7–11] over a large temperature and sulfur pressure range. Finally, the rate of manganese evaporation into vacuum from the surface of MnS scale in equilibrium with the metallic phase has been studied as a function of temperature[12,13] using Kofstad's method.[14]

Based on nonstoichiometry and electrical conductivity data, a defect structure model for $Mn_{1\pm y}S$ has been developed.[2,13] Sulfidation and evaporation rate measurements, in turn, have been utilized in calculating the self-diffusion coefficients of Mn in $Mn_{1\pm y}S$ over the phase field of this compound. It should be noted, however, that the results of these calculations have not been proved experimentally because the self-diffusion measurements in sulfides in equilibrium with sulfur vapor are much more difficult than in corresponding oxides. In fact, the only sulphide in which the self-diffusion rates of cations and anions have been studied systematically is the nonstoichiometric ferrous sulphide.[15]

The aim of the present paper is an attempt to determine the self-diffusion coefficient of manganese in manganous sulphide as a function of temperature and sulfur activity using the radioactive tracer method, and to compare the obtained experimental results with those calculated from manganese sulfidation and evaporation kinetics.

GENERAL REMARKS

It has been shown[1,2] that over the major part of the phase field, corresponding to higher sulfur activities, α-MnS which has the rocksalt structure, is a metal-deficit p-type semiconductor with the predominant defects being doubly ionized cation vacancies and electron holes ($Mn_{1-y}S$). At very low sulfur 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 doubly ionized interstitial cations and quasifree electrons as predominant defects ($Mn_{1+y}S$).[2,12,13] In the intermediate part of the phase field, in turn, near and at the stoichiometric composition, the defect structure of manganous sulphide is more complex and strongly dependent on temperature. It has been shown, finally, that the anion sublattice in the discussed sulphide is virtually ordered, the concentration of anion vacancies and interstitial anions being negligibly small as compared to the degree of cation sublattice disorder.[7]

Thus, all important defect equilibria in $Mn_{1\pm y}S$ can be described by the following quasichemical equations (Kröger-Vink[16] notation of defect is used throughout this paper):

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

$$1/2S_2(g) \rightleftarrows V_{Mn}^{\parallel}+2h^{\cdot}+S_S, \tag{2}$$

$$Mn_{Mn} \rightleftarrows Mn_i^{\cdot\cdot}+V^{\parallel}Mn \tag{3}$$

$$\text{``zero''} \rightleftarrows e^{-}+h^{\cdot}. \tag{4}$$

As the nonstoichiometry and thereby the defect concentration in manganous sulphide is very low,[1] their behavior could have been satisfactorily described in terms of point-defect thermodynamics.[17,18] Thus, for metal-deficit ($Mn_{1-y}S$) and metal-excess ($Mn_{1+y}S$) manganous sulphide

0163-1829/97/56(14)/8695(7)/$10.00

the following relationships describe the temperature and sulfur pressure dependence of predominant defects in this material:[2,13]

$$[\mathrm{Mn}_i^{\cdot\cdot}] \cong \frac{1}{2}[e^-] = 2.27 p_{S_2}^{-1/6} \exp\left(-\frac{151.0\ \mathrm{kJ/mol}}{\mathrm{R}T}\right) \quad (5)$$

and

$$[V_{\mathrm{Mn}}^{''}] \cong \frac{1}{2}[h^{\cdot}] = 6.99\times10^{-3} p_{S_2}^{1/6} \exp\left(-\frac{41.5\ \mathrm{kJ/mol}}{\mathrm{R}T}\right). \quad (6)$$

As can be seen, the pressure dependence of point-defect concentration in the discussed sulphide changes with increasing sulfur activity. In a very narrow range of low sulfur pressures, close to the Mn|MnS phase boundary doubly ionized interstitial cations are the predominant point defects, Eq. (1), and their concentration *decreases* with increasing sulfur activity, Eq. (5). At higher pressures, in turn, corresponding to the major part of the $\mathrm{Mn}_{1-y}\mathrm{S}$ phase field, doubly ionized cation vacancies constitute the prevailing point defects, Eq. (2), the concentration of which *increases* with increasing sulfur activity, Eq. (6).

In the transient pressure range, where the sulphide composition changes from metal-deficit ($\mathrm{Mn}_{1-y}\mathrm{S}$) to metal-excess ($\mathrm{Mn}_{1+y}\mathrm{S}$) the defect situations are strongly dependent on temperature because the enthalpy of Frenkel defect pair formation, Eq. (3), is considerably lower than that of intrinsic electronic disorder, Eq. (4). Consequently, at lower temperatures (<1100 K) intrinsic ionic disorder prevails, being independent of sulfur activity, Eq. (3), and at higher temperatures (>1100 K) intrinsic electronic defects predominate, Eq. (4), being again pressure independent. These two defect situations are described by the following relationships:[2,13]

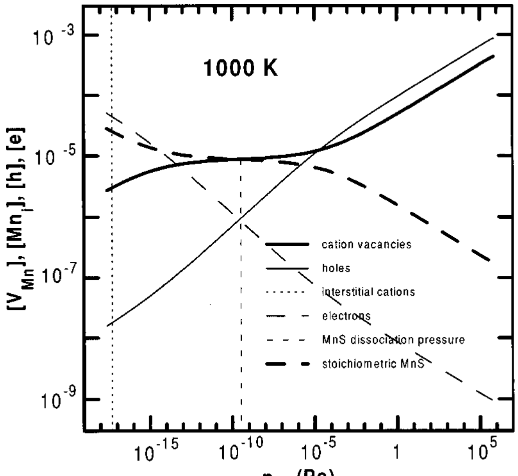

FIG. 1. Concentrations of ionic and electronic defects in $\mathrm{Mn}_{1\pm y}\mathrm{S}$ as a function of sulfur activity.

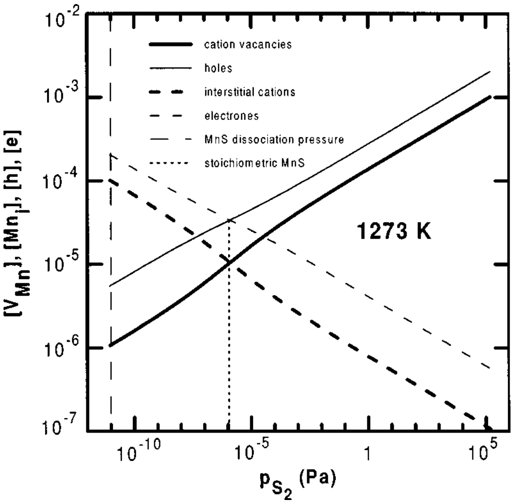

FIG. 2. Concentrations of ionic and electronic defects in $\mathrm{Mn}_{1\pm y}\mathrm{S}$ as a function of sulfur activity.

$$K_F = [V_{\mathrm{Mn}}^{''}][\mathrm{Mn}_i^{\cdot\cdot}] = 3.93\times10^{-10} \exp\left(-\frac{13.7\ \mathrm{kJ/mol}}{\mathrm{R}T}\right) \quad (7)$$

and

$$K_e = [h^{\cdot}][e^-] = 4.02\times10^{2} \exp\left(-\frac{281.4\ \mathrm{kJ/mol}}{\mathrm{R}T}\right), \quad (8)$$

where K_F and K_e denote equilibrium constants of defect reactions described by Eqs. (3) and (4), respectively. The influence of temperature on defect situations in $\mathrm{Mn}_{1\pm y}\mathrm{S}$ is shown in Figs. 1–3.

As the maximum deviation from stoichiometry of $\mathrm{Mn}_{1\pm y}\mathrm{S}$—even at very high temperatures ($T>1473$ K)—is very low ($y<0.01$) it could have been assumed that the mobility of point defects in this sulphide is independent of their concentration. Thus, the self-diffusion coefficient of Mn in $\mathrm{Mn}_{1\pm y}\mathrm{S}$, which is the product of the defect-diffusion coeffi-

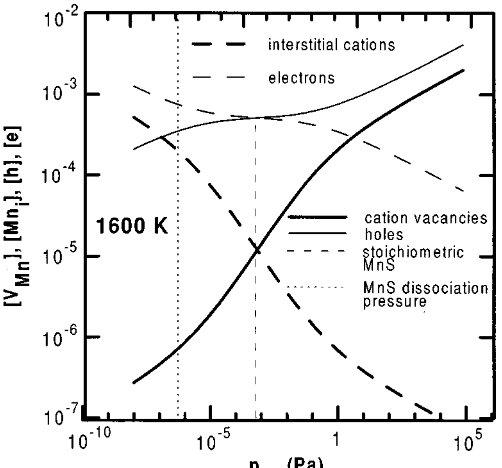

FIG. 3. Concentrations of ionic and electronic defects in $\mathrm{Mn}_{1\pm y}\mathrm{S}$ as a function of sulfur activity.

cients and their concentration,[17,18] should depend in the same way on sulfur activity as the concentration of defects. Consequently, in agreement with Eq. (5), at very low sulfur pressures, near the Mn|MnS phase boundary, the self-diffusion coefficient of manganese in metal-excess $\mathrm{Mn}_{1+y}\mathrm{S}$ ($D_{\mathrm{Mn}} = D^i_{\mathrm{Mn}}$) should be the following function of sulfur pressure and temperature:

$$\begin{aligned} D^i_{\mathrm{Mn}} &= D_i[\mathrm{Mn}_i^{\cdot\cdot}] \\ &= D_i^0 p_{S_2}^{-1/6} \exp\left(-\frac{E_D^i}{RT}\right), \end{aligned} \qquad (9)$$

where D_i denotes the defect-diffusion coefficient (diffusion coefficient of interstitial cations) which is only temperature dependent, and E_D^i is the activation energy of Mn self-diffusion being the sum of the enthalpy of defect (cation interstitials) formation and the activation enthalpy of their migration in $\mathrm{Mn}_{1+y}\mathrm{S}$ lattice.[13,18]

At higher pressures, in turn, in agreement with Eq. (6), the self-diffusion coefficient of manganese in metal-deficit $\mathrm{Mn}_{1-y}\mathrm{S}$ ($D_{\mathrm{Mn}} = D^v_{\mathrm{Mn}}$) should be described by the following relationship:

$$\begin{aligned} D^v_{\mathrm{Mn}} &= D_V[V_{\mathrm{Mn}}^{\|}] \\ &= D_V^0 p_{S_2}^{1/6} \exp\left(-\frac{E_D^V}{RT}\right), \end{aligned} \qquad (10)$$

where D_V denotes vacancy diffusion coefficient and E_D^V is again the activation energy of Mn self-diffusion, being the sum of the enthalpy of cation vacancy formation and the activation enthalpy of their migration in the $\mathrm{Mn}_{1-y}\mathrm{S}$ lattice.

The self-diffusion coefficient of Mn in $\mathrm{Mn}_{1-y}\mathrm{S}$ could be calculated as a function of temperature *and* sulfur activity from the parabolic rate constants of manganese sulfidation, and in agreement with Eq. (10), the following empirical relationship was obtained:[13]

$$D^V_{\mathrm{Mn}} = 9.81\times 10^{-5} p_{S_2}^{1/6} \exp\left(-\frac{121.0\ \mathrm{kJ/mol}}{RT}\right). \qquad (11)$$

The self-diffusion coefficient of Mn in metal-excess manganous sulphide ($\mathrm{Mn}_{1+y}\mathrm{S}$) could be calculated only as a function of temperature from evaporation rate measurements[12] carried out in equilibrium of $\mathrm{Mn}_{1+y}\mathrm{S}$ with manganese metal. Assuming, however, that D_{Mn} in $\mathrm{Mn}_{1+y}\mathrm{S}$ should decrease with increasing sulfur pressure in agreement with Eq. (9) the following quasitheoretical relationship has been obtained:[12]

$$D^i_{\mathrm{Mn}} = 1.72 p_{S_2}^{-1/6} \exp\left(-\frac{269\ \mathrm{kJ/mol}}{RT}\right). \qquad (12)$$

The overall self-diffusion coefficient of cations in $\mathrm{Mn}_{1\pm y}\mathrm{S}$, D_{Mn}, is at any sulfur pressure equal to the sum of self-diffusion coefficients due to the presence of both defects:

$$\begin{aligned} D_{\mathrm{Mn}} &= [V_{\mathrm{Mn}}^{\|}]D_V + [\mathrm{Mn}_i^{\cdot\cdot}]D_i \\ &= D^V_{\mathrm{Mn}} + D^i_{\mathrm{Mn}}. \end{aligned} \qquad (13)$$

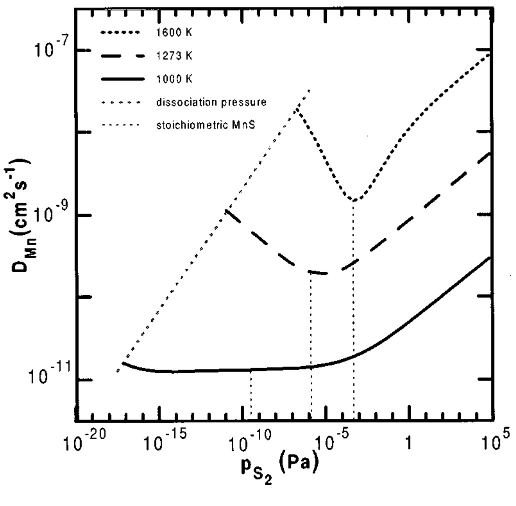

FIG. 4. Calculated dependence of manganese self-diffusion coefficient in manganous sulphide upon equilibrium sulfur pressure for several temperatures.

Thus, assuming relationship (13) and considering quasiempirical Eqs. (11) and (12), a diagram of D_{Mn} vs sulfur pressure for several temperatures has been constructed, Fig. 4. From the comparison of this diagram with those of the defect structure of $\mathrm{Mn}_{1\pm y}\mathrm{S}$ constructed for different temperatures (Figs. 1–3) it follows clearly that there is a very good agreement between the minimum concentration of point defects and the lowest diffusion rate of cations in the discussed sulphide. This fact may be considered as an indirect proof of the correct way of the calculations. However, all D_{Mn} values have not been determined experimentally and the dependence of this coefficient on sulfur activity is purely theoretical. In particular, the dependence of D_{Mn} on p_{S2} in the low sulfur pressure region, where interstitial cations and quasifree electrons predominate, results only from theoretical assumption and not from calculated values of D_{Mn} in $\mathrm{Mn}_{1+y}\mathrm{S}$, because D_{Mn} in this pressure range could have been calculated from Mn-evaporation kinetics for only one (lowest) sulfur pressure at a given temperature, equal to the dissociation pressure of the sulphide.[12,13]

Thus, not only the absolute values of the manganese self-diffusion coefficient in $\mathrm{Mn}_{1\pm y}\mathrm{S}$ but also its dependence on sulfur activity should be proven experimentally. This is the main purpose of this paper.

MATERIALS AND EXPERIMENTAL PROCEDURE

The starting material (α-MnS) has been obtained by sulfidation of spectrally pure manganese (Johnson & Matthey Ltd) in an apparatus described elsewhere.[19] Rectangular manganese samples of dimensions $2.0\times 1.5\times 0.3$ cm have been sulfidized completely at 1273 K in pure sulfur vapor at 10^2 Pa. Under these conditions compact, coarse-grained α-MnS scales have been formed, with grain size ranging from 400 up to 1800 μm. This material was ground and cold-pressed to get compact pellets 2.0 cm in diameter and 0.2 cm thick. They were then annealed at 1273 K for 48 h in sulfur vapor atmosphere at 5×10^3 Pa in order to obtain dense, coarse-grained samples. The average grain size of such well sintered, polycrystalline samples, with the density of 3.79 g cm^{-3}, was about 170 μm. Subsequently, the

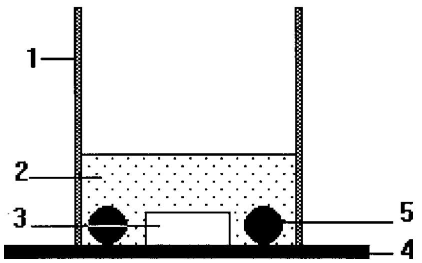

FIG. 5. The sample mounting unit, where: 1 indicates a metal tube; 2 indicates the resin; 3 indicates the sample; 4 indicates an abrasive disk, and 5 is the steel spheres.

samples were polished to get the surface flatness within ±1 μm. Finally, all the samples were preannealed at the same temperature and sulfur pressure at which the following diffusion experiment was to be carried out. This was done in order to establish the required defect concentration throughout the sample from the very beginning of subsequent diffusional annealing.

As the source of the radioactive manganese isotope, ^{54}Mn, a carrier-free solution of ^{54}MnCl$_2$ in ethyl alcohol was used. This isotope emits γ radiation with an energy of 0.83 MeV. The surface of the MnS samples, prepared in the way described above, was coated with ^{54}MnCl$_2$ solution and dried under infrared radiation. The activity obtained in the sample was about 11 μCi which corresponded to about 1 ng cm^{-2} of the ^{54}Mn isotope. Such a mass per unit surface area fulfilled the conditions of thin layer geometry. The diffusion experiments were performed by annealing the samples within evacuated and sealed quartz ampules at several temperatures (1073–1373) K and sulfur pressures (10^{-11}–10^{4}) Pa. The experimental procedure has been described elsewhere.[20] The source of the sulfur vapor in low-pressure experiments constituted the FeS$_2$-FeS mixture, and in high-pressure annealing it was liquid sulfur. After diffusional annealing the ampules were rapidly cooled and sample edges were cut to eliminate the possibility of additional radioactivity, originating from the sides of the specimen.

The ^{54}Mn penetration curves were obtained by the serial-sectioning technique. The samples were mounted in polyacryline resin together with three steel spheres having well-known diameter (0.4988 cm) as illustrated in Fig. 5.[21] The thin layers of the sulphide were then removed from the specimen surface by stepwise abrasion. The steel spheres were ground together with the specimen. To calculate the thickness of the removed sulphide layer the diameter of the cross section of the spheres were measured with the accuracy of ±1 μm. The residual activity of a specimen was counted in a constant geometry following the removal of each section. The NaJ(Tl) crystal scintillation counter was used. The statistical error was less then 1%. The counting rates were corrected for background and counter dead time. In order to avoid the influence of probable instability of the apparatus the counts were standardized to the counting rate of ^{54}Mn standard source.

RESULTS AND DISCUSSION

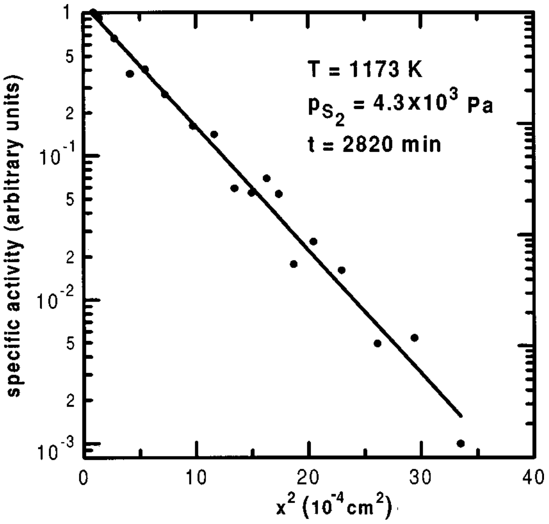

FIG. 6. Penetration depth profile of ^{54}Mn tracer atoms in Mn$_{1\pm y}$S after 47 h annealing in equilibrium with sulfur vapors.

The duration of diffusional annealing have been chosen in such a way that the thickness of the samples was always greater than the penetration depth of the tracer. This allows us to consider the discussed system in terms of the approximation to a semi-infinite solid. Thus, the solution of Fick's second law gives the following simple equation:[22]

$$C=\frac{C_0}{2\sqrt{\pi D_T t}}\exp\left(-\frac{x^2}{4D_T t}\right), \tag{14}$$

where C is the concentration of the tracer at a distance x from the sample surface; C_0 is its concentration on the surface before diffusional annealing, t is the time of the annealing, and D_T is the tracer-diffusion coefficient.

From Eq. (14) one obtains the linear relationship between ln$C$ and x^2:

$$\ln C=\ln\frac{C_0}{2\sqrt{\pi D_T t}}-\frac{x^2}{4D_T t}, \tag{15}$$

which is convenient for graphical interpretation.

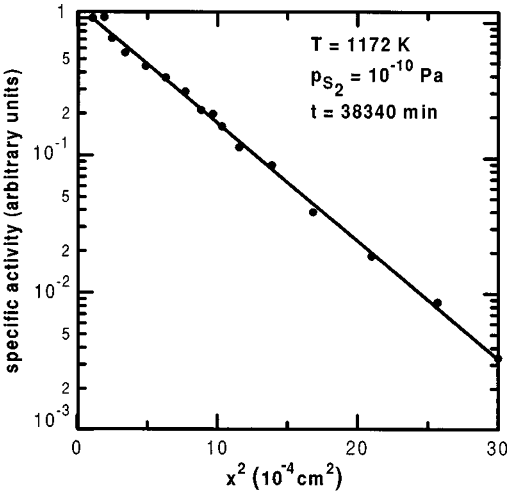

FIG. 7. Penetration depth profile of ^{54}Mn tracer atoms in Mn$_{1\pm y}$S after 639 h annealing in equilibrium with sulfur vapors.

TABLE I. Diffusion coefficients of Mn in $Mn_{1\pm y}S$.

p_{S2} (Pa)	T (K)	D_T (cm^2 s^{-1})	D_{Mn} (cm^2 s^{-1}) (measured) $f=0.7815$		D_{Mn} (cm^2 s^{-1}) (calculated)
4.3×10^3	1073	$(2.26\pm0.05)\times10^{-10}$	$(2.89\pm0.07)\times10^{-10}$		5.03×10^{-10}
4.3×10^3	1173	$(1.19\pm0.05)\times10^{-9}$	$(1.52\pm0.06)\times10^{-9}$		1.60×10^{-9}
4.3×10^3	1173	$(7.5\pm0.05)\times10^{-10}$	$(9.6\pm0.07)\times10^{-10}$		
4.3×10^3	1273	$(2.7\pm0.10)\times10^{-9}$	$(3.5\pm0.20)\times10^{-9}$		4.24×10^{-9}
4.3×10^3	1253	$(2.23\pm0.08)\times10^{-9}$	$(2.85\pm0.10)\times10^{-9}$		3.53×10^{-9}
4.3×10^3	1323	$(4.61\pm0.08)\times10^{-9}$	$(5.90\pm0.10)\times10^{-9}$		6.53×10^{-9}
4.3×10^3	1373	$(7.55\pm0.05)\times10^{-9}$	$(9.66\pm0.06)\times10^{-9}$		9.74×10^{-9}
4.3×10^3	1373	$(7.97\pm0.05)\times10^{-9}$	$(1.02\pm0.06)\times10^{-8}$		
6.2×10^2	1273	$(1.80\pm0.06)\times10^{-9}$	$(2.30\pm0.08)\times10^{-9}$		3.07×10^{-9}
53	1273	$(1.21\pm0.05)\times10^{-9}$	$(1.55\pm0.07)\times10^{-9}$		2.04×10^{-9}
53	1253	$(1.1\pm0.10)\times10^{-9}$	$(1.4\pm0.20)\times10^{-9}$		1.70×10^{-9}
10	1273	$(8.7\pm0.60)\times10^{-10}$	$(1.11\pm0.08)\times10^{-9}$		1.54×10^{-9}
			$f=0.6666$	$f=0.970$	
10^{-10}	1253	$(2.5\pm0.12)\times10^{-10}$	$(3.75\pm0.20)\times10^{-10}$	$(2.6\pm0.12)\times10^{-10}$	5.08×10^{-10}
10^{-10}	1210	$(1.15\pm0.09)\times10^{-10}$	$(1.7\pm0.10)\times10^{-10}$	$(1.19\pm0.09)\times10^{-10}$	2.20×10^{-10}
10^{-10}	1172	$(5.5\pm0.20)\times10^{-11}$	$(8.2\pm0.30)\times10^{-11}$	$(5.7\pm0.20)\times10^{-11}$	1.10×10^{-10}
10^{-10}	1123	$(1.42\pm0.06)\times10^{-11}$	$(2.13\pm0.09)\times10^{-11}$	$(1.46\pm0.06)\times10^{-11}$	5.28×10^{-11}
10^{-11}	1253	$(3.6\pm0.25)\times10^{-10}$	$(5.4\pm0.40)\times10^{-10}$	$(3.7\pm0.26)\times10^{-10}$	7.42×10^{-10}
10^{-11}	1273	$(5.7\pm0.20)\times10^{-10}$	$(8.6\pm0.30)\times10^{-10}$	$(5.9\pm0.20)\times10^{-10}$	1.10×10^{-9}

As the concentration of the radioactive tracer is directly proportional to its specific activity, $C=\text{const}(\partial I/\partial x)_t$, the tracer-diffusion coefficient may easily be calculated from the slope of such straight lines, Eq. (15), using the following relationship:[23]

$$D_T=-\frac{1}{4t}\left(\frac{\partial x^2}{\partial\ \ln(\partial I/\partial x)}\right)_t, \tag{16}$$

where I is the counting rate. Figures 6 and 7 illustrate some of the obtained penetration depth profiles for the diffusion of the ^{54}Mn tracer in $Mn_{1\pm y}S$.[21,24] As can be seen, at all temperatures and sulfur pressures straight lines have been obtained enabling the self-diffusion coefficients of manganese in metal-excess and metal-deficit manganous sulphide to be calculated from Eq. (16). The results of these calculations are summarized in Table I and plotted as a function of temperature and sulfur pressure in Figs. 8 and 9. It follows clearly from these plots that in agreement with the defect model of $Mn_{1\pm y}S$ the mechanism of Mn self-diffusion at very low sulfur pressures is different from that observed in the high-pressure region. At low pressures, namely, the rate of self-diffusion *decreases* with increasing sulfur pressure, as predicted for metal-excess $Mn_{1+y}S$ sulphide, Eq. (9), and at higher pressures it *increases*, that is again in agreement with the defect-structure model for metal-deficit $Mn_{1-y}S$, Eqs. (10) and (11). In addition, the activation energy of Mn self-

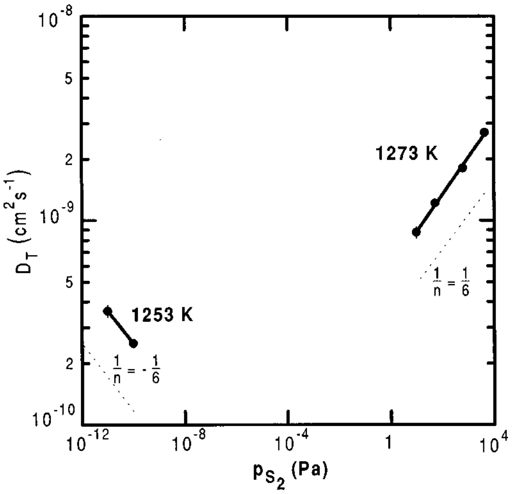

FIG. 8. Pressure dependence of ^{54}Mn tracer-diffusion coefficient in $Mn_{1\pm y}S$ (double logarithmic plot).

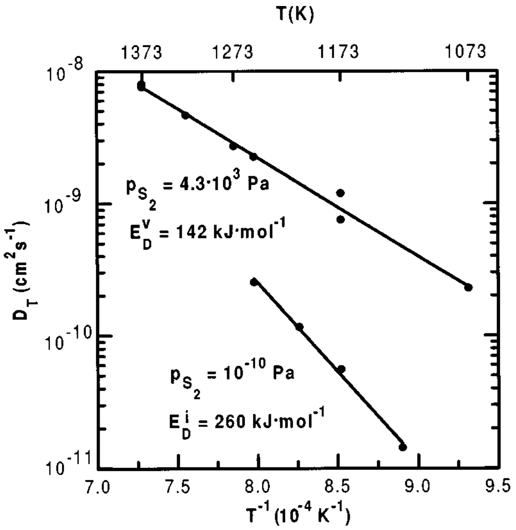

FIG. 9. Temperature dependence of the ^{54}Mn tracer-diffusion coefficient in $Mn_{1\pm y}S$ for two different sulfur pressures.

diffusion in $Mn_{1+y}S$ is much higher than that in $Mn_{1-y}S$, being in excellent agreement with the value calculated from evaporation kinetic measurements, Eq. (12). This energy in the high-pressure region ($Mn_{1-y}S$) is also in qualitative agreement with that calculated from manganese sulfidation kinetics, Eq. (11). Finally, the pressure dependence of the self-diffusion coefficient in metal-excess and metal-deficit manganous sulphide determined experimentally is in good agreement with that calculated from evaporation and sulfidation kinetics, Eqs. (11) and (12).

The question then arises, whether not only temperature and pressure dependence of the self-diffusion rate, but also absolute values of the manganese self-diffusion coefficient calculated from kinetic experiments are in agreement with those determined experimentally. In order to make such a comparison, diffusion coefficients obtained from tracer experiments, i.e., tracer-diffusion coefficients D_T must be recalculated into ''real'' self-diffusion coefficients D_{Mn} by taking into account the correlation effect.[25–27] These two diffusion coefficients are interrelated by the correlation factor:

$$D_{Mn}=D_T/f, \tag{17}$$

where f denotes the correlation factor, which values depend on mechanisms of diffusion and the crystal structure of a given solid. In the case under discussion the different correlation factors should be applied for vacancy and *interstitial* mechanisms of diffusion (a simple interstitial mechanism of diffusion consisting of successive jumps of interstitial cations from one initial position to another should *a priori* be excluded because of purely geometrical reasons[18]). In the case of the vacancy mechanism, consisting of Mn^{+2} ions jumping from the lattice sites into neighboring cation vacancies, the correlation factor for a face-centered-cubic lattice of α-MnS assumes the value: $f=0.7815$.[28,29] In the case of interstitial diffusion, the situation is more complex, because at least two different mechanism of this process are possible. In both of them the elementary act of diffusion consists of displacement of a lattice atom by its interstitial neighbor into the interstitial position. However this process may take place in two ways. The displacing and displaced atoms can move along the straight line (collinear interstitialcy) and the correlation factor for the discussed crystal structure assumes the value $f=0.6666$.[28,29] If, on the other hand, the displaced atom moves to the interstitial position at an angle to the direction of the displacing atom (noncollinear interstitialcy) the correlation factor $f=0.970$.[30] Using these three correlation factors and Eq. (17) tracer-diffusion coefficients of ^{54}Mn in $Mn_{1\pm y}S$ have been recalculated into self-diffusion coefficients of cations in this sulphide. The results of these calculations have been plotted as a function of temperature and sulfur activity in Fig. 10 on the background of data obtained from sulfidation[31] and evaporation kinetics.[12] As can be seen, over the whole phase field of $Mn_{1\pm y}S$ the calculated values of D_{Mn} in this sulphide are in agreement with those determined experimentally. It should be stressed however, that D_{Mn} values obtained from tracer data by assuming the collinear interstitialcy mechanism ($f=0.6666$) in metal-excess $Mn_{1+y}S$ are in better agreement with calculated D_{Mn} coefficients from the manganese evaporation kinetics, than those obtained for noncollinear diffusion mechanism ($f=0.970$). These results strongly suggest that the self-diffusion of cations in metal-excess manganous sulfide proceeds by the collinear interstitialcy mechanism. The satisfactory agreement between calculated and experimentally determined D_{Mn} values, and the fact that the pressure dependence of the self-diffusion rate in both metal-excess and metal-deficit manganous sulphide agrees very well with the defect model of this sulphide, strongly suggests that at high temperatures ($T>1000$ K) grain-boundary diffusion does not play an important role in the overall matter transport in this polycrystalline material. Consequently, self-diffusion coefficients of cations reported in the present work describe volume (lattice) diffusion. In order to support this conclusion autoradiographs of surfaces normal to the diffusion direction have been taken from several samples at different penetration depths. If grain-boundary diffusion would prevail, the network of grain boundaries would be visible on the autoradiographs taken on highly sensitive films. The autoradiographs showed uniform blackening of the film, clearly indicating that in agreement with the above conclusion, grain-boundary diffusion of cations in $Mn_{1\pm y}S$ can be neglected. In fact, this conclusion follows also from the character of ^{54}Mn-tracer distribution in α-MnS samples after diffusional annealing. Fisher[32] showed that when diffusion along grain boundaries predominates, the logarithm of tracer concentration C is a linear function of x and not of x^2, as it has been found in our experiments (Figs. 6 and 7).

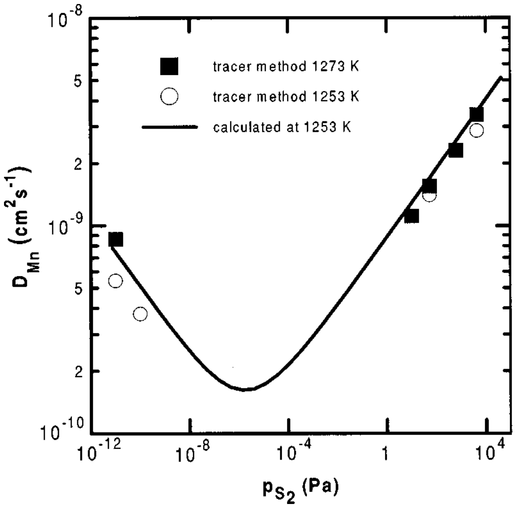

FIG. 10. The calculated and measured values of the manganese self-diffusion coefficient in α-MnS at 1253 and 1273 K.

CONCLUSIONS

The results obtained in the present work allow the following conclusions to be formulated:

(1) Self-diffusion of cations in nonstoichiometric manganous sulphide at temperatures exceeding 1000 K proceeds mainly through point defects, i.e., by volume diffusion. In agreement with the defect structure model of $Mn_{1\pm y}S$ two different mechanisms of self-diffusion may be distinguished. In the very narrow part of the phase field, close to the Mn/MnS phase boundary, i.e., at very low sulfur activities, doubly ionized interstitial cations and quasi-free electrons are the

prevailing defects in $\mathrm{Mn}_{1+y}\mathrm{S}$ and the self-diffusion proceeds by the collinear interstitialcy mechanism, consisting of pushing the cations from their normal lattice sites into neighboring interstitial positions (both the displacing and displaced ions moving along a straight line). At higher sulfur activities, when doubly ionized cation vacancies and electron holes constitute the predominant disorder in $\mathrm{Mn}_{1-y}\mathrm{S}$ the self-diffusion of cations proceeds by simple vacancy mechanism consisting of Mn^{2+} ions jumping from the lattice sites into neighboring cation vacancies.

(2) The satisfactory agreement between experimentally determined self-diffusion coefficients of Mn in $\mathrm{Mn}_{1\pm y}\mathrm{S}$ and those calculated from manganese sulfidation and evaporation kinetics clearly indicates that these kinetic methods can successfully be utilized in studying the transport properties of transition-metal sulfides and oxides. The first of these two methods, called in the literature the Fueki-Wagner method, consisting of calculating the D_{Me} values from parabolic kinetics of sulfidation or oxidation of a given metal, has already been proved on Fe-$\mathrm{Fe}_{1-y}\mathrm{S}$-S (Ref. 33) and Co-$\mathrm{Co}_{1-y}\mathrm{O}$ (Ref. 34) systems. However, this method cannot be utilized at low oxidant pressures, close to the dissociation pressure of the compound forming the scale. The diffusion-evaporation method, on the other hand, developed by Kofstad,[14] enables the self-diffusion coefficient D_{Me} to be calculated for equilibrium pressure only, equal to the dissociation pressure of the compound forming the scale. This method has been used by Kofstad[35] in determining the self-diffusion coefficient of manganese in manganous oxide and by Danielewski and Mrowec[12] in manganous sulphide. However, none of these results have been confirmed experimentally by direct-tracer experiments. Thus, the results described in the present paper constitute an experimental verification of Kofstad's diffusion-evaporation method. Excellent agreement of D_{Mn} values calculated from the kinetics of manganese evaporation with those determined experimentally in $\mathrm{Mn}_{1+y}\mathrm{S}$ clearly indicates that this method can successfully be used in studying the transport properties of transition-metal sulfides and oxides.

ACKNOWLEDGMENTS

This work was partially supported by the State Committee for Scientific Research and the University of Mining and Metallurgy, Grants No. 11.220.01, 11.163.1, and 11.160.169.

---

[1] H. Rau, J. Phys. Chem. Solids **39**, 339 (1978).
[2] M. Danielewski and S. Mrowec, Solid State Ion. **17**, 29 (1985).
[3] K. Fueki, Y. Oguri, and T. Makaibo, Denki Kagaku Oyobi Kogyo Butsuri **38**, 758 (1970).
[4] H. Le Brusq and J. P. Delmaire, Rev. Inst. Hautes Temp. Refract. **11**, 193 (1974).
[5] J. Rasneur and D. Carton, C. R. Acad. Sci. II, Mech. Phys. Chim. Sci. Univers **290**, 405 (1980).
[6] J. Rasneur and N. Dhebormez, C. R. Acad. Sci. II, Mech. Phys. Chim. Sci. Univers **292**, 593 (1981).
[7] M. Danielewski, Oxid. Met. **25**, 51 (1986).
[8] M. Danielewski, H. J. Grabke, and S. Mrowec, Corros. Sci. **28**, 1107 (1988).
[9] F. A. Erlefaie and W. W. Smeltzer, Oxid. Met. **26**, 267 (1981).
[10] M. Perez and J. P. Larpin, Oxid. Met. **21**, 229 (1984).
[11] P. Papaiacovou, H. J. Schmidt, H. Erhart, and H. H. Grabke, Werkstoffe Korros. **38**, 498 (1987).
[12] M. Danielewski and S. Mrowec, Solid State Ion. **17**, 319 (1985).
[13] S. Mrowec, M. Danielewski, and H. J. Grabke, J. Mater. Sci. **25**, 537 (1990).
[14] P. Kofstad, J. Phys. Chem. Solids **44**, 129 (1983).
[15] H. Condit, R. R. Hobbins, and C. E. Birchenall, Oxid. Met. **8**, 409 (1974).
[16] F. Kröger, *The Chemistry of Imperfect Crystals* (North-Holland, Amsterdam, 1964).
[17] P. Kofstad, *Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides* (Wiley, New York, 1972), p. 80.
[18] S. Mrowec, *Defects and Diffusion in Solids* (Elsevier, Amsterdam, 1980), p. 193.
[19] M. Danielewski and S. Mrowec, J. Therm. Anal. **29**, 1021 (1984).
[20] J. Gilewicz-Wolter and Z. Żurek, Solid State Commun. **88**, 279 (1993).
[21] J. Gilewicz-Wolter, Solid State Commun. **93**, 61 (1995).
[22] S. Mrowec, *Defects and Diffusion in Solids* (Ref. 18), p. 361.
[23] P. L. Gruzin, Dokl. Akad. Nauk SSSR **86**, 289 (1952).
[24] J. Gilewicz-Wolter and A. Ochoński, Solid State Commun. **99**, 273 (1996).
[25] K. Compaan and Y. Haven, Trans. Faraday Soc. **52**, 586 (1956).
[26] A. Lidiard, Philos. Mag. **46**, 1218 (1955).
[27] J. Bardeen and C. Herring, *Imperfections in Nearly Perfect Crystals* (Wiley, New York, 1952), p. 261.
[28] K. Compaan and Y. Haven, Trans. Faraday Soc. **52**, 786 (1956).
[29] K. Compaan and Y. Haven, Trans. Faraday Soc. **54**, 1498 (1958).
[30] J. N. Mundy, in *Fast Ion Transport in Solids Electrodes and Electrolytes*, edited by P. Vashishta, J. N. Mundy, and G. K. Shenoy (North-Holland, New York, 1979).
[31] M. Danielewski and S. Mrowec, Solid State Ion. **17**, 41 (1985).
[32] J. Fisher, J. Appl. Phys. **22**, 74 (1951).
[33] M. Danielewski and S. Mrowec, Solid State Ion. **17**, 319 (1985).
[34] S. Mrowec and K. Przybylski, Oxid. Met. **11**, 365 (1977); **11**, 365 (1977).
[35] P. Kofstad, Solid State Ion. **12**, 101 (1984).