Chalcogen Interdiffusion in the System Pb(S, Se)

Volkmar Leute, Harald Böttner, Heinrich Schmidtke
Institut für Physikalische Chemie, Universität Münster

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From the sulfur- and selenium-concentration profiles recorded by an electron microprobe the chalcogen interdiffusion coefficient of the system Pb(S, Se) is determined as a function of mass fraction c_{PbSe} and temperature. Undoped crystals and Pb- or chalcogen-saturated crystals are studied. The dependence of the interdiffusion coefficient on the deviation from stoichiometry shows that in the chalcogen-saturated part of the system the calcogen interdiffusion proceeds via chalcogen interstitials, whereas in the Pb-saturated part of the system the chalcogens diffuse via chalcogen vacancies. For pure PbSe it is shown that these vacancies are doubly ionized. The activation entropy of the diffusion of the chalcogens depends linearly on the ratio of activation enthalpy to solidus temperature.

This paper reports on diffusion- and charge carrier density-measurements which were carried out in order to understand the diffusion mechanism of the chalcogens in the system Pb(S, Se).

Experimental

As initial materials PbS-powder (99,999%)* as well as elementary lead (99,999%)* and elementary selenium (99,999%) are used. PbSe is prepared by heating a weighted, stoichiometric mixture of the elements, sealed in an evacuated quartz ampoule. When the reaction is complete, the molten compound is homogenised by gently shaking for about 5 minutes. The compounds PbS and PbSe are purified by sublimation in the dynamical vacuum at 900 °C. Substances prepared in this way have the composition of minimum vapour pressure ("undoped chalcogenides").

Crystals of PbS and PbSe are grown in double walled quartz ampoules by the Bridgman method. The growing rate amounts to 6 mm/h, the temperature gradient to 10 K/cm. The crystal rods are cleaved to pieces of several mm^3 or sawn to slices of about 1 mm thickness. Lead saturated crystals (**Pb**S or **Pb**Se) are produced by heating the undoped crystals together with a heterogeneous mixture of Pb and polycrystalline chalcogenide, chalcogen saturated crystals (PbS or PbSe) by heating together with a mixture of sulfur or selenium and polycrystalline chalcogenide. The annealing process is carried out at the same temperature at which the crystals will be used afterwards for diffusion experiments. The annealing time is the higher the lower the temperature of the following diffusion experiments will be (3 h at 1000 °C; 500 h at 500 °C). After having quenched the crystals to room temperature no precipitations of elements can be seen in the microscope.

Reprint requests to Dr. V. Leute, Institut für Physikalische Chemie, Schloßplatz 4, D-4400 Münster.

* Koch-Light.

Diffusion Experiments

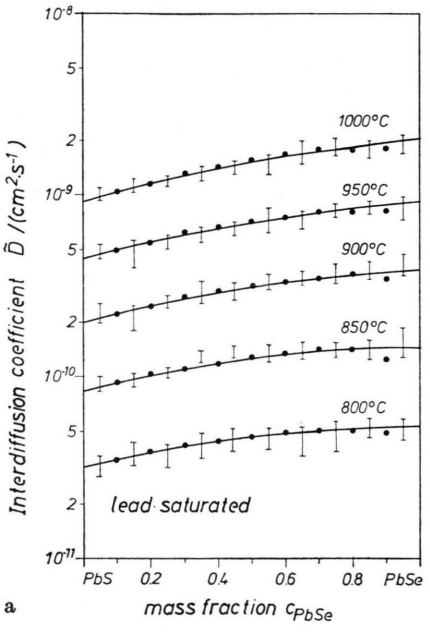
Pb-saturated, chalcogen-saturated, and undoped diffusion couples are prepared by pressing together the polished surfaces of the pretreated PbS- and PbSe-crystals within a matrix of polycrystalline PbSe, which has the same composition as the PbSe-crystal. A pressure of about 9 kbar is used. The diffusion couples are heated in sealed quartz ampoules. Even at diffusion temperatures of 1000 °C the annealing time takes at least 30 min. Therefore the time needed to reach the annealing temperature can be neglected. When diffusion experiments with Pb- or chalcogen-saturated samples are carried out, a mixture of Pb and PbSe or Se and PbSe is always added to the diffusion couple, in order to stabilize the vapour pressure, corresponding to the three phase equilibria.

After having ground and polished the annealed samples the concentration distribution of the chalcogens in the diffusion zone is measured by an electron microprobe (accelerating voltage 25 kV; sample current $\approx 10^{-7}$ A, conditions of spectrometers see Table 1). From the measured and calibrated diffusion profiles the interdiffusion

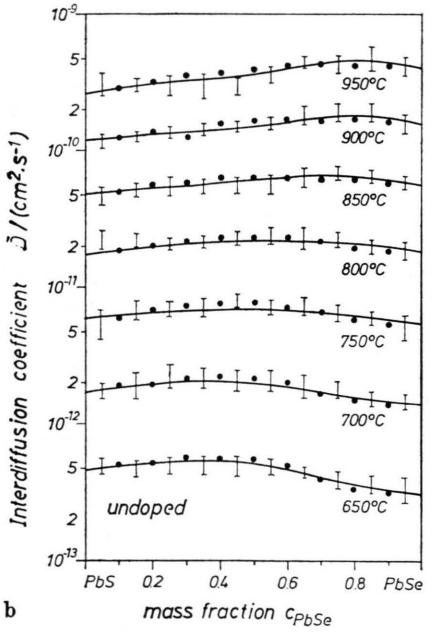
Table 1. Spectrometer conditions for the measurement of the characteristic X-ray intensities in the system Pb(S, Se).

Element	Crystal	Line
Pb	LiF	L_α 1. Order
	KAP	M_α 1. Order
S	KAP	K_α 1. Order
Se	LiF	K_α 1. Order
	Quartz	K_α 2. Order

coefficients of the chalcogens as a function of the alloy composition are calculated using a Boltzmann-Matano method, modified by den Broeder [1]. In the Figs. 1a, b, c the interdiffusion coefficients of the chalcogens are plotted as function of the mass fraction c_{PbSe} of PbSe for several diffusion temperatures. The error bars noted in the figures correspond to 95 percent confidence inter-



a



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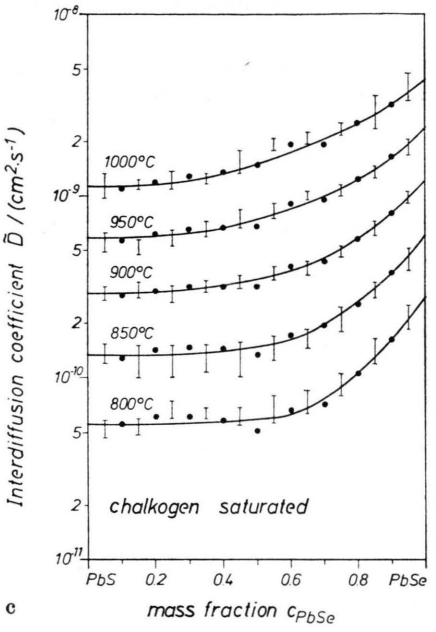

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Fig. 1. Interdiffusion coefficients of the chalcogens in the system Pb(S, Se) for differently doped diffusion couples. Full line: calculated from Eq. (1) using ΔH- and $\tilde{D}_0$-values from Figs. 2 and 3; error bars: 95% confidence limits $N \geq 6$; dots: values calculated from Equation (3).

vals. Assuming that the temperature dependence of the interdiffusion coefficient corresponds to the Arrhenius relation

$$\tilde{D}(c) = \tilde{D}_0(c) \exp[-\Delta H(c)/RT] \quad (1)$$

the concentration dependent values of $\Delta H(c)$ and $\tilde{D}_0(c)$ are calculated by a least squares fit of all interdiffusion coefficient values. In the Figs. 2 and 3 the values of ΔH and $\tilde{D}_0$ are plotted in dependence of the PbSe-mass fraction c_{PbSe}. The extrapolated boundary values are compared in Table 2.

Comparison of Fig. 2 with Fig. 3 reveals a strong correlation between $\tilde{D}_0$ and ΔH. Plotting $\lg \tilde{D}_0$ against $\Delta H(c)/T_s(c)$, where $T_s(c)$ is the solidus

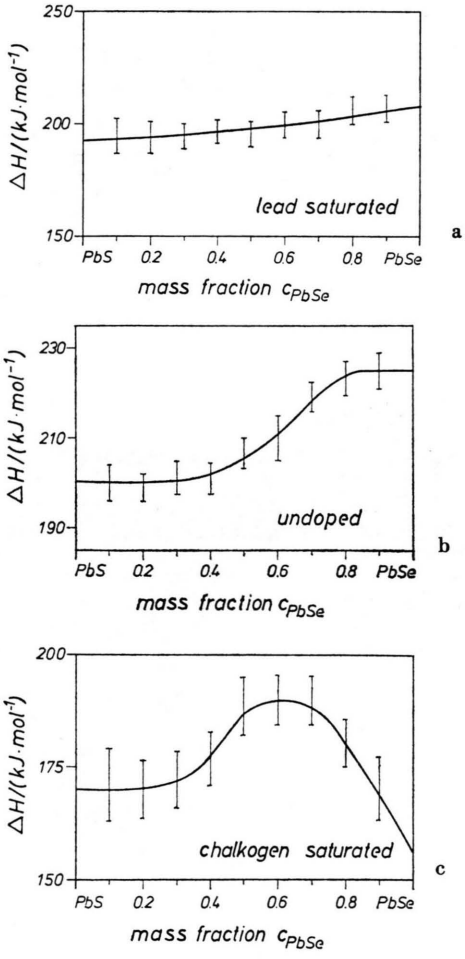

Fig. 2. Activation enthalpies of the chalcogen interdiffusion in the system Pb(S, Se) for differently doped diffusion couples. Error bars: rms-errors of a least squares fit according to Eq. (1) using the $\tilde{D}$-values of all temperatures.

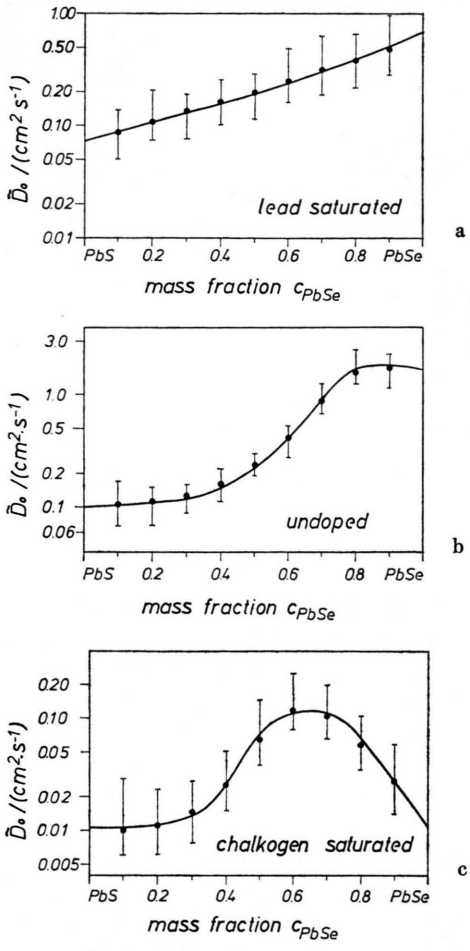

Fig. 3. $\tilde{D}_0$-values for the chalcogen interdiffusion in the system Pb(S, Se) for differently doped diffusion couples. Error bars: rms-errors of a least squares fit according to Eq. (1) using the $\tilde{D}$-values of all temperatures. Dots: $\tilde{D}_0$-values calculated from Equation (2).

temperature, yields a straight line as well in the metal saturated as in the undoped system. In the chalcogen saturated system two linear branches are needed to describe the correlation between

Table 2. Extrapolated boundary values of ΔH and $\tilde{D}_0$ for differently doped PbS- and PbSe-crystals.

Substance	ΔH/kJ · mol^{-1}	$\tilde{D}_0$/cm^2 · s^{-1}
PbS	192	0.07
PbS	200	0.10
PbS	170	0.01
PbSe	208	0.70
PbSe	225	1.66
PbSe	156	0.01

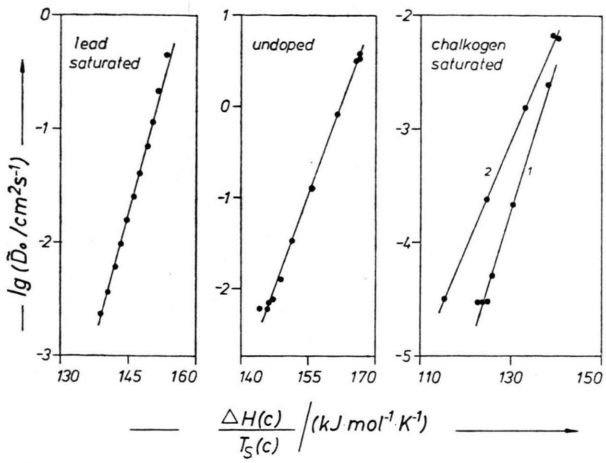

Fig. 4. Linear correlationship between $\lg \tilde{D}_0(c)$ and $\Delta H(c)/T_s(c)$.

$\tilde{D}_0(c)$ and $\Delta H(c)/T_s(c)$ (Figures 4a, b, c). The concentration dependence of $T_s(c)$ of the semiconductor alloy $Pb(S_{(1-c)}Se_c)$ is taken from the paper of Strauss and Harman [2]. The values of the parameters $\lg A$ and b in Eq. (2), calculated from the linear plots of $\lg \tilde{D}_0$ against $\Delta H/T_s$, are listed in Table 3.

$$\lg\left(\frac{\tilde{D}_0}{\mathrm{cm^2\,s^{-1}}}\right) = \lg\left(\frac{A}{\mathrm{cm^2\,s^{-1}}}\right) + 0{,}434\,\frac{b}{R}\,\frac{\Delta H(c)}{T_s(c)}. \quad (2)$$

This linearity shows that in the Pb(S, Se)-system as in a series of other quasibinary semiconductor alloys [3, 4, 5], the activation entropy of diffusion depends linearly on the ratio of activation enthalpy and solidus temperature. The concentration- and temperature-dependence of the chalcogen interdiffusion coefficient can be described in good approximation by the equation

$$\tilde{D}(c, T) = A \exp\left\{\frac{\Delta H(c)(b\,T - T_s(c))}{R\,T_s(c)\,T}\right\}. \quad (3)$$

$\tilde{D}$ values calculated according to Eq. (3) are plotted in Fig. 1 as dots.

Hall-Effect Measurements

To measure the carrier densities of metal- and chalcogen-saturated PbS- and PbSe-crystals, a DC-Hall effect apparatus is used. Cylindrical crystal slices with a radius of 3 mm and a thickness of 1 mm are used to measure the Hall effect. The measurements are carried through at room temperature at quenched samples using the van der Pauw method with 4 contacts [6]. In order to check the reproducibility of the measurements and to see if equilibrium conditions are reached, several crystals are successively saturated with lead, than with chalcogen, than with lead again and once more with chalcogen. The values measured for the same kind of doping show satisfying accordance. The experimental values of the carrier densities as function of the temperature at which equilibrium was established are listed in Table 4. In Fig. 5a and b these values are compared with the values of other authors [7, 8, 9].

Discussion

The comparison of the diffusion coefficients for a given temperature measured on differently doped systems shows that in the whole investigated temperature region the following relation holds

$$\tilde{D}_{Ch}^{X} > \tilde{D}_{Ch}^{p\text{-min}} < \tilde{D}_{Ch}^{M} \quad (4)$$

(X = chalcogen saturated; M = metal saturated).

Table 4. Carrier densities for lead saturated and chalcogen saturated PbS and PbSe.

T [°C]	PbS n [cm^{-3}]	PbS p [cm^{-3}]	PbSe n [cm^{-3}]	PbSe p [cm^{-3}]
500	$6{,}2 \cdot 10^{18}$		$3{,}0 \cdot 10^{18}$	
600	$8{,}5 \cdot 10^{18}$	$2{,}8 \cdot 10^{18}$	$4{,}8 \cdot 10^{18}$	$7{,}7 \cdot 10^{18}$
700	$1{,}4 \cdot 10^{19}$	$5{,}0 \cdot 10^{18}$	$8{,}1 \cdot 10^{18}$	$1{,}1 \cdot 10^{19}$
800	$2{,}0 \cdot 10^{19}$	$5{,}9 \cdot 10^{18}$	$1{,}1 \cdot 10^{19}$	$1{,}4 \cdot 10^{19}$
900	$1{,}9 \cdot 10^{19}$		$1{,}2 \cdot 10^{19}$	$1{,}3 \cdot 10^{19}$
1000			$1{,}3 \cdot 10^{19}$	$9{,}3 \cdot 10^{19}$

Table 3. Parameters $\lg(A)$ and b from Equation (2).

	Pb-saturated	undoped	chalcogene-saturated	
Concentration range	$0 \leq c_{PbSe} \leq 1$	$0 \leq c_{PbSe} \leq 1$	$0 \leq c_{PbSe} \leq 0.5$	$0.5 \leq c_{PbSe} \leq 1.0$
$\lg (A/\mathrm{cm^2 \cdot s^{-1}})$	− 10.19	− 9.53	− 6.64	− 8.91
b	1.24	1.12	1.07	0.78

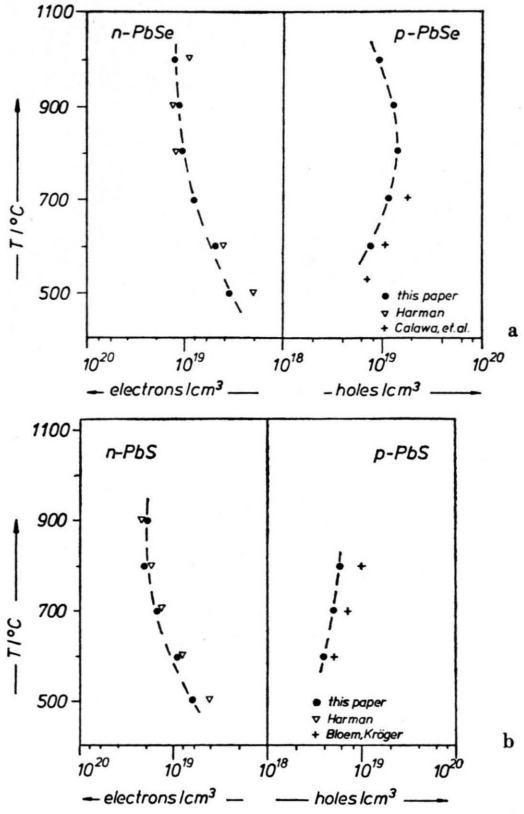

Fig. 5. Charge carrier densities from Hall-Effect measurements.

According to this relation the chalcogen interdiffusion coefficient in the undoped system ($\tilde{D}_{\mathrm{Ch}}^{\mathrm{p\text{-}min}}$) is always lower than in the Pb- or chalcogen-saturated system.

The chalcogen interdiffusion coefficient can be described by a superposition of an interstitial- and a vacancy-term:

$$\tilde{D}_{\mathrm{Ch}} = \tilde{D}_{X_i}[X_i] + \tilde{D}_{V_X}[V_X]\,, \tag{5}$$

($\tilde{D}_{X_i}$, $\tilde{D}_{V_X}$ = diffusivities of interstitials i or vacancies V).

The probability $[X_i]$ that a chalcogen particle X resides in the interstitial lattice increases proportionally to the square root of the chalcogen partial pressure

$$1/2\, X_2(g) \rightarrow X_i\,; \quad [X_i] = K_X\, p_{X_2}^{1/2}\,. \tag{6}$$

The probability $[V_X]$ that a site in the chalcogen sublattice is vacant is linked to $[X_i]$ via the Anti-Frenkel defect equilibrium

$$\begin{aligned} &[X_X] + [V_i] \rightarrow [X_i] + [V_X]\,; \\ &[X_i]\,[V_X] = K_{AF}\,. \end{aligned} \tag{7}$$

This equilibrium causes a decrease of vacancy concentration with increasing chalcogen partial pressure:

$$[V_X] = (K_{AF}/K_X)\, p_{X_2}^{-1/2}\,. \tag{8}$$

Therefore we can qualitatively understand the dependence of the chalcogen interdiffusion coefficient on the chalcogen partial pressure, that means its dependence on doping, by assuming an Anti-Frenkel-disorder and by taking the diffusivities $\tilde{D}_{X_i}$ and $\tilde{D}_{V_X}$ for independent on doping.

In order to get a quantitative description we have to make assumptions on the effective charges of the defects and on the nature of the majority defects.

Measurements of the carrier densities at room temperature on PbS and PbSe are best explained by the assumption of effective singly ionized donors and acceptors [10]. For diffusion conditions (800 °C$< T <$ 1000 °C), however, one has also to take into consideration that the vacancies and Pb-interstitials might be doubly ionized. Probably the chalcogen interstitials are also partially ionized at these temperatures, but it is most improbable that the voluminous chalcogen ions in the interstitial lattice have appreciable mobility. Therefore we assume that only the effective neutral chalcogen interstitials contribute to diffusion. At a given temperature and composition the density of these neutral defects is proportional to $\sqrt{p_{X_2}}$ (see Equation (6)).

Investigations at room temperature lead to the result that in the Pb-chalcogenides the whole region of existence can be described by two regions of different neutrality condition, the n-region with electron and the p-region with holes as majority carriers [11]. If we transfere this result to the high-temperature region, that means, if we assume that also at high temperatures the region of pure intrinsic conductivity ($n = p$) is negligible small, we get two regions with the neutrality conditions

$$n = q([V_x^q] + [\mathrm{Pb}_i^q])\,; \quad p = q[V_{\mathrm{Pb}}^{q'}]\,. \tag{9}$$

For simplification we assumed that both types of vacancies and the lead interstitials have the same amount of charge q. The development of the outlined defect model yields for the two defects, which contribute to the chalcogen interdiffusion, the following dependencies on the chalcogen partial pressure:

$$[X_i] = \alpha \cdot p_{X_2}^{1/2}\,; \quad [V_x^q] = \beta \cdot p_{X_2}^{-1/2(q+1)}\,. \tag{10}$$

These relations are the same as well for the n-region as for the p-region. Therefore the dependence of the chalcogen interdiffusion coefficient on the chalcogen partial pressure for the whole region of non-stoichiometric PbS or PbSe can be described by

$$\tilde{D}_{\mathrm{Ch}} = a\, p_{X_2}^{1/2} + b p_{X_2}^{-1/2(q+1)}$$
$$\text{with} \quad a = \alpha \tilde{D}_{X_i} \quad \text{and} \quad b = \beta \tilde{D}_{V_X}. \qquad (11)$$

Measurements of $\tilde{D}_{\mathrm{Ch}}$-values for maximum and minimum equilibrium partial pressure as well as for minimum total pressure were reported in the experimental part of this paper. The corresponding partial pressures of sulfur or selenium for the pure chalcogenides PbS and PbSe are known from the literature [12]. Extrapolation of the $\tilde{D}_{\mathrm{Ch}}(c_{\mathrm{PbSe}})$-curves up to the boundaries $c_{\mathrm{PbSe}} = 0$ and $c_{\mathrm{PbSe}} = 1$ yields the tracer diffusion coefficients of Se in PbS and S in PbSe. For these coefficients the dependence on chalcogen partial pressure is evidently the same as for the interdiffusion coefficient:

$$D^*_{\mathrm{Se(PbS)}} = a_{\mathrm{PbS}}\, p_{S_2}^{1/2} + b_{\mathrm{PbS}}\, p_{S_2}^{-1/2(q+1)} \qquad (12\mathrm{a})$$

$$D^*_{\mathrm{S(PbSe)}} = a_{\mathrm{PbSe}}\, p_{Se_2}^{1/2} + b_{\mathrm{PbSe}}\, p_{Se_2}^{-1/2(q+1)} \qquad (12\mathrm{b})$$

The boundary values D^*_{Se} and D^*_{S} (Table 5) are calculated according to Eq. (1) using the extrapolated ΔH and $\tilde{D}_{\mathrm{O}}$-values of Table 2. From these D^*-values and the corresponding partial pressure p_{X_2}, taken from literature [12], the parameters a and b are calculated (Table 6). The curves $D^*_{\mathrm{Se(PbS)}}$ versus p_{S_2} and $D^*_{\mathrm{S(PbSe)}}$ versus p_{Se_2}, corresponding to these parameters and for defect charges $q = 1$ and $q = 2$, are plotted in Fig. 6a and b. The extrapolated $\tilde{D}^{\mathrm{p\text{-}min}}_{X_2}$-values of the undoped systems

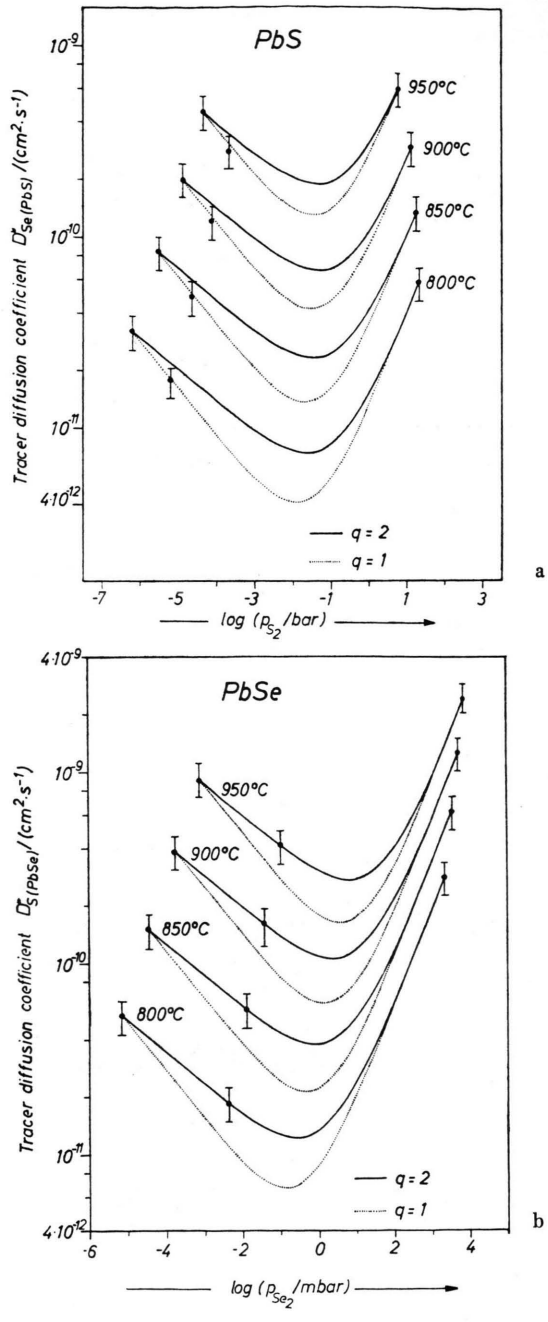

Fig. 6. Chalcogen tracer diffusion coefficients in dependence on chalcogen partial pressure and temperature. Full and dotted lines calculated according to Eqs. (12a) and (12b). The dots correspond to the values of Table 5; the estimated errors of 20% are greater than the errors indicated in Figure 1.

Table 5. Tracer diffusion coefficients $D^*_{\mathrm{S(PbSe)}}$ and $D^*_{\mathrm{Se(PbS)}}$ for differently doped PbS and PbSe.

T [°C]	$D^{*\mathrm{M}}_{\mathrm{S(PbSe)}}$ [cm² · s⁻¹]	$D^{*\mathrm{p\text{-}min}}_{\mathrm{S(PbSe)}}$ [cm² · s⁻¹]	$D^{*\mathrm{X}}_{\mathrm{S(PbSe)}}$ [cm² · s⁻¹]	$D^{*\mathrm{M}}_{\mathrm{Se(PbS)}}$ [cm² · s⁻¹]	$D^{*\mathrm{p\text{-}min}}_{\mathrm{Se(PbS)}}$ [cm² · s⁻¹]	$D^{*\mathrm{X}}_{\mathrm{Se(PbS)}}$ [cm² · s⁻¹]
800	$5{,}3 \cdot 10^{-11}$	$1{,}86 \cdot 10^{-11}$	$2{,}81 \cdot 10^{-10}$	$3{,}20 \cdot 10^{-11}$	$1{,}77 \cdot 10^{-11}$	$5.71 \cdot 10^{-11}$
850	$1{,}5 \cdot 10^{-10}$	$5{,}71 \cdot 10^{-11}$	$6.13 \cdot 10^{-10}$	$8{,}35 \cdot 10^{-11}$	$4{,}83 \cdot 10^{-11}$	$1{,}33 \cdot 10^{-10}$
900	$3{,}86 \cdot 10^{-10}$	$1{,}60 \cdot 10^{-10}$	$1{,}25 \cdot 10^{-9}$	$2{,}00 \cdot 10^{-10}$	$1{,}20 \cdot 10^{-10}$	$2{,}90 \cdot 10^{-10}$
950	$9{,}24 \cdot 10^{-10}$	$4{,}10 \cdot 10^{-10}$	$2{,}40 \cdot 10^{-9}$	$4{,}50 \cdot 10^{-10}$	$2{,}80 \cdot 10^{-10}$	$5{,}91 \cdot 10^{-10}$
1000	$2{,}06 \cdot 10^{-9}$		$4{,}40 \cdot 10^{-9}$	$9{,}45 \cdot 10^{-10}$		$1{,}14 \cdot 10^{-9}$

Table 6. Parameters a and b of Eqs. (12a) and (12b) for singly ($q=1$) and doubly ($q=2$) ionized defects.

PbS	$q=1$		$q=2$	
T [°C]	a [$cm^2 \cdot s^{-1} \cdot bar^{-1/2}$]	b [$cm^2 \cdot s^{-1} \cdot bar^{1/4}$]	a [$cm^2 \cdot s^{-1} \cdot bar^{-1/2}$]	b [$cm^2 \cdot s^{-1} \cdot bar^{1/6}$]
800	$1{,}26 \cdot 10^{-11}$	$9{,}04 \cdot 10^{-13}$	$1{,}23 \cdot 10^{-11}$	$2{,}97 \cdot 10^{-12}$
850	$3{,}22 \cdot 10^{-11}$	$3{,}48 \cdot 10^{-12}$	$3{,}11 \cdot 10^{-11}$	$1{,}00 \cdot 10^{-11}$
900	$7{,}94 \cdot 10^{-11}$	$1{,}18 \cdot 10^{-11}$	$7{,}56 \cdot 10^{-11}$	$3{,}04 \cdot 10^{-11}$
950	$2{,}37 \cdot 10^{-10}$	$3{,}67 \cdot 10^{-11}$	$2{,}21 \cdot 10^{-10}$	$8{,}46 \cdot 10^{-11}$

PbSe	$q=1$		$q=2$	
T [°C]	a [$cm^2 \cdot s^{-1} \cdot bar^{-1/2}$]	b [$cm^2 \cdot s^{-1} \cdot bar^{1/4}$]	a [$cm^2 \cdot s^{-1} \cdot bar^{-1/2}$]	b [$cm^2 \cdot s^{-1} \cdot bar^{1/6}$]
800	$6{,}03 \cdot 10^{-12}$	$2{,}73 \cdot 10^{-12}$	$5{,}99 \cdot 10^{-12}$	$7{,}34 \cdot 10^{-12}$
850	$1{,}05 \cdot 10^{-12}$	$1{,}17 \cdot 10^{-11}$	$1{,}04 \cdot 10^{-11}$	$2{,}73 \cdot 10^{-11}$
900	$1{,}76 \cdot 10^{-11}$	$4{,}43 \cdot 10^{-11}$	$1{,}74 \cdot 10^{-11}$	$9{,}12 \cdot 10^{-11}$
950	$2{,}81 \cdot 10^{-11}$	$1{,}50 \cdot 10^{-10}$	$2{,}76 \cdot 10^{-11}$	$2{,}75 \cdot 10^{-10}$

(Table 5) are also shown in these figures and one can see that for PbSe in the whole temperature region between 800 °C and 950 °C these values can best be described by the assumption of doubly ionized chalcogen vacancies ($q=2$).

In the case of PbS we can not decide between singly and doubly ionized vacancies, because there is only a small difference in S_2-pressure for metal-saturated and for undoped samples.

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