JOURNAL OF MATERIALS SCIENCE 7 (1972) 807–812

Diffusion of some impurities in zinc sulphide single crystals

V. A. WILLIAMS*
International Centre for Theoretical Physics, Trieste, Italy

Using a lapping and surface-counting method, the diffusion of Mn and Au are studied and compared with the self-diffusion of S in ZnS^c. In all three cases diffusion constants exhibit a distribution over the samples used; however, by considering a large number of sample batches, average activation energies of 3.15, 2.46 and 1.16 eV have been obtained, respectively, for sulphur, manganese and gold.

1. Introduction

Previous studies of the luminescence and opto-electronic phenomena in ZnS have been mostly on polycrystalline systems. But with the increasing availability of single crystals, attention is now switching to the study of such phenomena in single crystals. It has usually been assumed that interpretation of phenomena observed in crystalline powder systems can be simply extrapolated to single crystals, or that simplified experimental systems would emerge with the use of single crystals [1].

However, the simplified experimental systems expected to emerge as a result of the switch-over to single crystals have not so far materialized because of the still unsolved problems of producing structurally pure crystals (or of quality comparable to currently available silicon or germanium crystals), as well as problems attendant on processing the crystals for various purposes. One of these problems is to effect controlled diffusion of specified impurities into the crystal lattice.

It is well known that in the $A_{II}B_{VI}$ family of compounds, of which ZnS is a prominent member, incorporation of foreign atoms, because of the ionicity content of the bonding, generally proceeds by means of charge compensation mechanism even in the presence of native point defects in the crystal matrix. This charge compensation requirement is independent of the particular diffusion mechanism, i.e. whether by an interstitial or substitutional process. Other factors which will affect the diffusion are structural defects, such as stacking faults, line dislocations and grain boundaries, and the directions of these relative to the initial direction of the impurity concentration gradient.

A detailed investigation of diffusion processes in ZnS single crystals would provide useful data for the controlled incorporation of specified impurities in ZnS, resulting in better interpretability of observed phenomena in ZnS systems. However, such a study would involve detailed correlation of defect distributions on the observed diffusion in the crystals. This is rather involved. In this paper preliminary results are presented of an attempt to attack this problem systematically.

In this work it has been endeavoured to minimize the charge compensation problem by incorporating the diffusions via a charge-compensated dissociative two-component phase. For example, for Au in a chloride complex we have [2]

$$\left(1 - \frac{3\delta}{2}\right) \mathrm{ZnS} + \frac{\delta}{2}\,\mathrm{ZnCl_2} + \frac{\delta}{2}\,\mathrm{Au_2S} \rightarrow (1 - \delta)\,\mathrm{ZnS} + \delta\,\mathrm{AuCl} = \mathrm{Zn_{(1-\delta)}Au_\delta S_{(1-\delta)}Cl_\delta} \qquad (1)$$

although for manganese the situation is somewhat simpler because

$$(1 - \delta)\,\mathrm{ZnS} + \delta\,\mathrm{MnS} \rightarrow \mathrm{Zn_{(1-\delta)}\,Mn_\delta S} \qquad (2)$$

and since MnS is practically isomorphous with ZnS^c the diffusion of Mn in the lattice should be practically analogous with the self-diffusion of either constituents of ZnS.

---

*On leave of absence from Department of Physics and Electronics, University of Ife, Ile-Ife, Nigeria.

2. Experimental method

Platelets 10 × 7 × 1.5-2 mm were cut from large lumps, 5 to 10 g weight, of Eagle-Picher (USA) ZnS single crystals. These crystals which are cubic were known generally to contain twins, stacking faults and other polytypic formations [3]. The platelets were not cut to specific orientations, neither were attempts made to check or identify specific faults in any platelet. However, a large number of platelets were cut, selected and randomly grouped into batches. The platelets were lapped parallel (parallelism $\approx$ 20 light bands) and polished using fine polishing grade alumina powder. Final thicknesses were about 1 mm.

The radio-active isotopes were supplied by the Radio Chemical Centre, Amersham. Mn^{57} was contained in a highly concentrated solution of the chloride in HCl, Au^{195} in high concentration in aqua regia and S^{35} also in high concentration in benzene. Drops of these, respectively, were placed on one surface of platelets of ZnS crystals and spread so as to leave a peripheral skirt 1.5 mm wide of the edges of the surface. These were then kept for about 24 to 36 h to dry in a high-purity argon atmosphere (BOC argon, 99.9995% pure) which was being slowly evacuated. Painting of the surface in this way was repeated in each case, resulting in a uniformly glazed appearance of the platelet's surface.

Batches of seven to eight platelets all glazed with the same isotope were placed on a quartz tray and preheated in a quartz furnace tube continuously evacuated (pressure $\approx 10^{-5}$ Torr) at about 250° C to dissociate and drive off water of crystallization and any absorbed water vapour. The trays were then withdrawn to the cold zone of the furnace tube while the temperature of the hot zone was raised under vacuum to a pre-selected temperature at which the diffusion was to be effected. The furnace was controlled by a proportional controller employing a chromel-alumel thermocouple and was capable of maintaining a selected temperature ± 0.5° C. At the selected temperature the furnace tube was flushed with argon and then filled up to 3 atm pressure. The tray containing the specimens was then pushed to the hot zone for the diffusion run, typically for about 6 h. The samples were quenched by again withdrawing them to the cold part of the furnace before the furnace was shut off.

Specimens were then washed in alcohol and glued onto aluminium discs 1 in. in diameter previously parallel-lapped to better than 20 light bands. These discs were designed to fit into special jigs which enabled the thickness of the platelets to be measured accurately using a Wayne-Kerr electronic micrometer with a resolution of better than 10^{-8} m (> 1 µin.). These discs were further employed to obtain parallel lapping of the platelets for the activity versus depth measurements. After each lapping operation, using an oil lapping compound, specimens, before thickness measurement and surface counting for the residual activity, were washed in toluol and rinsed with a mixture of ether and alcohol. For surface counting, specimens were placed on a pedestal of adjustable height. The pedestal plus specimen are in turn placed in an Ecko Type N619 lead sample oven with shielded G.M. Tube Holder Type N620 housing an end-window geiger-muller counter. The height of the pedestal was adjusted against a fixed stop such that the clearance between the counter window and specimen surface was always about 1 mm. Counts were made against fixed-time periods, the mean being taken over a number of such counting periods to obtain a measure of the activity.

3. Results

We assume with Rupp *et al* [5] that we have a thin instantaneous plane source resulting in a concentration profile of the form in this case of

$$c[x, Dt] = \frac{K_0}{2(4\pi Dt)^{\frac{1}{2}}} \exp\left[-\frac{x^2}{4Dt}\right] \qquad (3)$$

where K_0 is a constant of the source. Since Mn^{57} and Au^{195} emit γ-radiation, the activity measured at any surface represents the residual activity in the sample and so the concentration gradient at any given depth would be proportional to $d[A(x)]/dx$ where $A(x)$ is the measured surface activity at a depth x. A plot of $A'(x)$ versus x^2 would then give a slope corresponding to $-1/4Dt$ from which the diffusion constant D is obtained.

However, since S^{35} is a β-emitter, $A(x)$ is proportional to the concentration gradient c at any depth and so the slope of log $A(x)$ versus x^2 plot would give the value of D.

Accordingly, after a least squares smoothing of all the $A(x)$ data for each temperature, those for Mn and Au were numerically differentiated, again using a least squares method. From the plots of $A'(x)$ versus x^2 for these diffusors D-values for each sample were obtained.

It was observed that there was a spread of

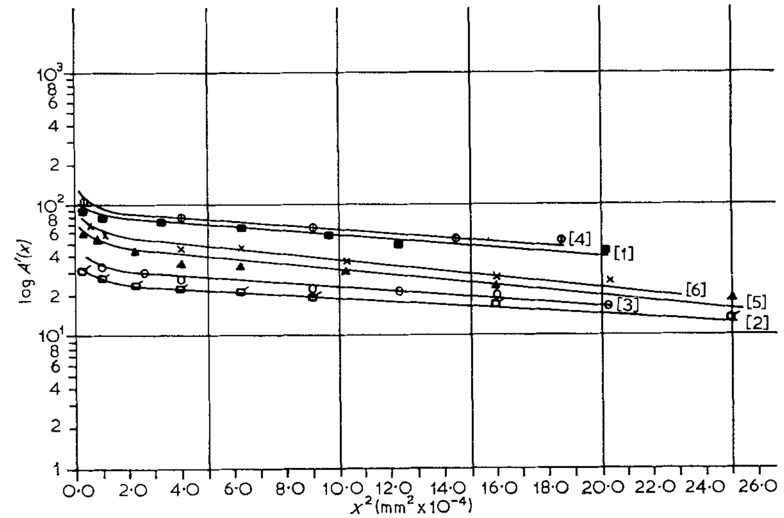

Figure 1 Log A^1 (x) versus x^2 for Mn for a batch of platelets at 700°C showing a more uniform behaviour (see Table I column 1). The vertical displacements of the curves are the result of numerical differentiation of $A(x)$. The $A(x)$ data when smoothed were weighted to a common value of A_0. The same applies to curves in Fig. 2.

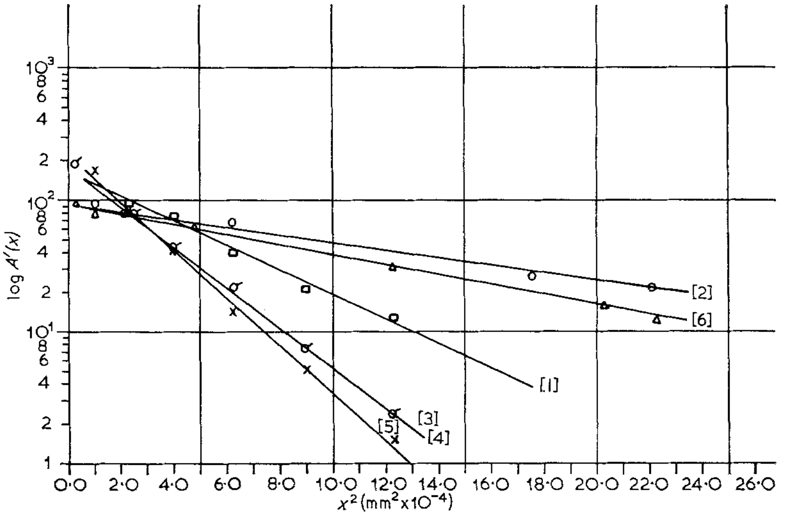

Figure 2 Log A^1 (x) versus x^2 for Mn for a batch of platelets at 500°C with [2] and [6] showing gross deviations from the others (see Table I education 2).

D-values over the samples in a batch. Some batches had relatively little spread while in some batches one, two or more platelets exhibited gross deviations from the average. Fig. 1 illustrates the situation where platelets are well behaved while Fig. 2 shows a case where samples exhibited gross differences. Table I column 1 gives the D-values from Fig. 1 while column 2 gives those from Fig. 2. From the detailed analysis of a large number of batches, at each temperature of diffusion (temperatures chosen were 800, 700, 600 and 500°C) it became possible to select averagely well-behaved results from those that grossly deviated, and use these to calculate average D values from which Arrhenius plots could be made in order to obtain values of the activation energies. A comparison of Arrhenius plots for all three diffusors are given

TABLE I Comparison of diffusion constants for two batches of which one contains grossly deviated specimens

D_i cm²/sec	1 Mn 700°C	2 Mn 500°C
D_1	5.621×10^{-10}	$*3.395 \times 10^{-11}$
D_2	7.142×10^{-10}	13.156×10^{-11}
D_3	7.075×10^{-10}	$*2.178 \times 10^{-11}$
D_4	5.994×10^{-10}	$*2.178 \times 10^{-11}$
D_5	5.314×10^{-10}	$*1.24 \times 10^{-11}$
D_6	3.915×10^{-10}	11.197×10^{-11}
	Mean = 5.84×10^{-10}	Mean (all values) = 5.56×10^{-11}
	Standard deviation = 1.10108×10^{-10}	Standard deviation (all values) 4.75570×10^{-11}
		Mean of four starred values = 2.25×10^{-11}
		Standard deviation of four starred values = 4.75570×10^{-11}
		(It is clearly better to discard the grossly deviated results in this batch.)

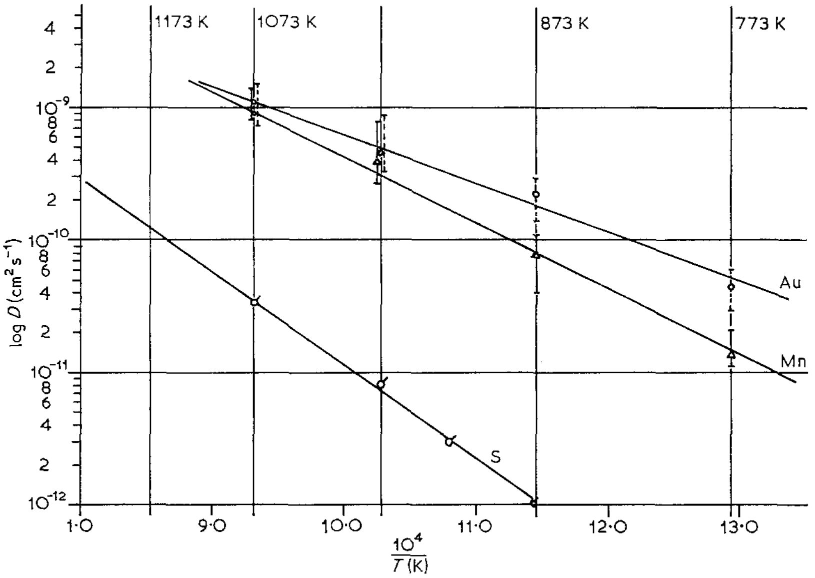

Figure 3 Arrhenius plots for Au, Mn and S after averaging over selected batches. Typical spreads are indicated for Au and Mn.

TABLE II Activation energy and D_0 values obtained for Mn, Au and S.

Diffuser	Q (eV)	D_0 (cm² s⁻¹)
Mn	2.46	2.3×10^3
Au	1.16	$1{:}75 \times 10^{-4}$
S	3.15	2.16×10^4

in Fig. 3. Table II gives the Q and D_0 values, respectively, from the Arrhenius plots and the usual equation

$$D = D_0 \exp\left(\frac{-Q}{k_B T}\right), \qquad (4)$$

4. Discussion

First of all we compare our data with what little data there is available from other workers, principally Aven and Halsted [5], Blount, Marlor, and Bube [6], and Nelkowski and Bollman [7], as shown in Table III. The work of Aven and Halsted was, however, mainly on ZnSe, with only a passing mention of the diffusion coefficient of Cu in ZnS at one temperature. The results of Nelkowski and Bollman, and of Blount *et al*, are thus more useful for our comparisons. It is interesting that in their experiments Nelkowski and Bollman had attempted to eliminate the probable effects of stacking disorders by attempting to make the

TABLE III Comparison of results from different workers quoted in Refs. 6 and 7 with present work.

Reference	Diffuser	D_0(cm^{2}s^{-1})	Q (eV)	
[6]	S	$8.2 \times 10^{5*}$	3.4 eV	The work of Ref. 5 dealt mostly on ZnSe with which the diffusion coefficient of Cu in ZnS is compared at 500°C where it was found to be one half that in ZnSe, i.e. 1.5×10^{-9} cm^{2}s^{-1} at 500°C.
[7]	In	30.0	2.2	
	Cu	2.6×10^{-3}	0.79	
Present work	Mn	2.3×10^{2}	2.46	
	Au	1.75×10^{-4}	1.16	
	S	2.16×10^{4}	3.15	

*This result was calculated from the given data for S, i.e. $D_{800°C} = 7 \times 10^{-11}$ cm^2 s^{-1}.

direction of the concentration profiles perpendicular to fault planes. On the other hand, Blount *et al* have not been so specific as to the structural purity or otherwise of their crystal specimens. Nevertheless, the results show a good measure of agreement. D_0 was calculated from the given value of $D_{800°C}$ and the activation energy.

Our results for the self-diffusion of sulphur agree generally with those of Blount *et al*; we may use the value of the activation energy obtained as a datum for discussing the other results. First, the results for Mn are discussed. The value of the activation energy would suggest Mn is a slow diffuser. It would be expected that the self-diffusion activation energy for Zn in ZnS would be less than for S (e.g. ionic radii for S^{2-} and Zn^{2+} are respectively 1.82 and 0.83Å) [8]. Since Mn^{2+} ($r_{io} = 0.83$Å) substitutes directly for Zn^{2+} ($r_{io} = 0.83$Å) in an isomorphic mixture in the ZnS lattice, this value should be comparable with the self-diffusion activation energy for Zn in ZnS. The value of 1.16 eV for Au in ZnS suggests a different mechanism of incorporation from that of Mn. In this respect it is a little difficult to reconcile Nelkowski's result for Cu in ZnS with this on a purely mechanical picture of the diffusion process. However, the electronegativity difference between the incorporated ion and its opposite species in the crystal would also affect the required activation energy for motion through the crystal. This is probably why, for an expected similar mechanism of diffusion in ZnS for Cu and Au, the activation energies should be so different (0.79 eV for Cu fc. 1.16 eV for Au).

Only tentative conclusions can be drawn at the moment as to the predominating processes of diffusion for the two metals. Clearly both processes would be influenced by the density of zinc vacancies in the crystal. It is also difficult to envisage any other mechanism for Mn other than substitutional via zinc vacancies. With Au, however, the interstitial mechanism is probably accompanied by substitutional diffusion via zinc vacancies according to the chemical reaction [9].

$$\text{interstitial impurity} + \text{vacancy} \rightleftharpoons \text{substitutional impurity} \quad (5)$$

This is a transition from one configuration of the impurity state to another, and would obviously involve extra energy.

The effect of the presence of dislocation and fault planes is indicated in the crystal specimens showing gross deviations in their $A'(x)$ versus x^2 plots and consequently larger values of D (see for example Fig. 2). In the present state of the art currently available ZnS are known to have a wide variety of structural defects such as twins, stacking faults and other defects arising from the tendency to polytypism. Where fault planes intersect the direction of the impurity concentration gradient faster diffusion along the defect planes than in the bulk will occur [10]. Quantitative estimates of the diffusion rate along the defects can be made, but it is first necessary to locate and identify the defect and its density.

Finally, it has been shown that meaningful results can be obtained by using conventional techniques in the study of diffusion processes in ZnS crystals. However, to categorize the diffusion mechanism for particular impurity types requires the development of methods of distinguishing between substitutional and interstitial configurations of an impurity in ZnS and the role of native defects in the crystal. These problems are currently engaging our attention.

Acknowledgements

The experimental work was carried out at the University of Ife, Nigeria, and the calculations and data analysis were carried out at the

International Centre for Theoretical Physics, Trieste. The author wishes to express sincere thanks to Professor D. F. Ojo of the Physics Department, University of Ife, for facilities provided, Professor Abdus Salam, the International Atomic Energy Agency and UNESCO for hospitality at the International Centre for Theoretical Physics, and also to the Swedish International Development Authority for making possible the author's Associateship at the ICTP.

References

1. V. A. WILLIAMS, Ph.D. thesis, Manchester University, 1963.
2. F. A. KROGER, *Proc. IRE* **43** (1955) 1941.
3. D. E. MASON, private communications, Manchester University, 1968.
4. W. RUPP, U. ERMERT, and R. SIZMANN, *Phys. Stat. Sol.* (1969) 509.
5. M. AVEN and E. E. HALSTED, *Phys. Rev.* **137A** (1965) 228.
6. G. H. BLOUNT, G. A. MARLOR, and R. H. BUBE, *J. Appl. Phys.* **38** (1967) 3795.
7. H. NELKOWSKI and G. BOLLMAN, *Z. Naturforsch.* **A24** (1969) 1302.
8. G. WYCKOFF, "Crystal Structures" (Interscience Publishers, New York, 1960), Vol. 4, p. 521.
9. F. C. FRANK and D. TURNBULL, *Phys. Rev.* **104** (1956) 617.
10. G. S. KULIKOV and E. I. GIUARGIZOV, *Fiz. Tver. Tela.* **8** (1966) 3344.

Received 30 September 1971 and accepted 21 January 1972.