Self-Transport in Polycrystalline Zn and Pb *

P. Thernqvist and A. Lodding

Physics Department, Chalmers University of Technology, Gothenburg, Sweden

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Electrotransport has been studied in pure zinc and lead, using a non-isothermal inert marker technique. The mass transport is directed towards the anode. The effective valence of a diffusing atom (at 0.95 T_m) is for Zn about -3, for Pb -40. The results are in fair agreement with those obtained by a different technique. No definite evidence of thermotransport has been found.

The method employed in this study of atom transport in pure solid metals was similar in principle to that first used by Wever [1] and then developed by Huntington and co-workers [2, 3]. The motion of inert markers on the surfaces of DC- or AC-carrying metal rods was observed under a microscope. A temperature gradient was maintained by forced cooling of the rod ends. For a general account of the method and underlying principles, one may refer to a review article by Huntingon [4]. The mass flow can be shown to be oppositely directed and simply proportional to the marker motion. The special modifications employed in the present work have been described in a detailed article on electrotransport in In [5]. The most important improvement on the In work consisted in the employment of gettered argon atmosphere in the cell.

The results are shown in Fig. 1, expressed in transport numbers (defined as the ratio of mass transport velocity to electron cloud velocity, positive if metal ions move towards cathode), calculated on the arbitrary assumption that the effective number of conduction electrons per atom is 2 in Zn, 4 in Pb. Comparison has been made with the results obtained earlier by Kuzmenko et al. [6], who used a radioactive and weighing technique in essentially isothermal measurements. The main aim of the present work was in fact to get a notion of the relative accuracy of the two methods and in particular to check the earlier results in Zn and Pb, as they are relevant to the question of the charge carrier sign. In Zn, especially, with a large positive Hall coefficient, one would have expected a mass motion towards the cathode, as observed by Wever [7] in Fe. However, it is obvious from Fig. 1 that self-transport in Zn and Pb is anode-directed, and the present results show rather a good agreement with those by Kuzmenko. In ref. [6], measurements were recorded only for 2 temperatures for each metal, with a considerable spread of results; in Fig. 1 the mean values are shown

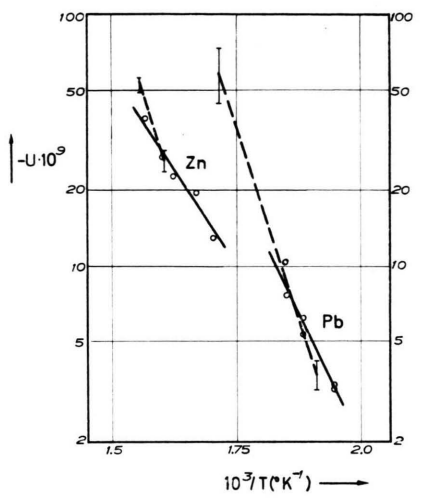

Fig. 1. Self-transport numbers of Zn and Pb as functions of inverse temperature. $U = -v_m/v_e$, where v_m is the mass transport velocity and v_e the "electron cloud" velocity. It has been arbitrarily assumed that Zn contains 2, Pb 4 conduction electrons per atom. Dashed lines and corresponding error margins: from ref. [6].

with their standard deviations. For the upper temperature in Pb, only one reading is given in ref [6], and the error shown in Fig. 1 is the algebraic mean of the percentual errors at the lower temperature. It can be noticed that the present method yields somewhat less steep lines; this tendency has been seen in all metals where non-isothermal marker type results have been compared with those obtained by isothermal means (see summary of results up to 1963 in ref. [5], cf. also ref. [8]).

Fig. 2 shows the "effective valence" z^* of diffusing Zn- and Pb-ions, as computed from the present results and from ref. [6]. This entity is defined from

$$v_m = (D/f\,k\,T)\;E\,e\,z^*, \qquad (1)$$

where v_m is the mass transport velocity, D the self-diffusion coefficient, f a correlation factor, k Boltzmann's constant, E the field and e electronic charge. The advantage of expressing the results in z^* is that no assumption is needed concerning the effective number z of free electrons. If such an assumption can be made with reasonable certainty, as in the case of the noble metals and alkalis, the "effective resistivity" ϱ^* per lattice defect can be calculated according to a formula due to

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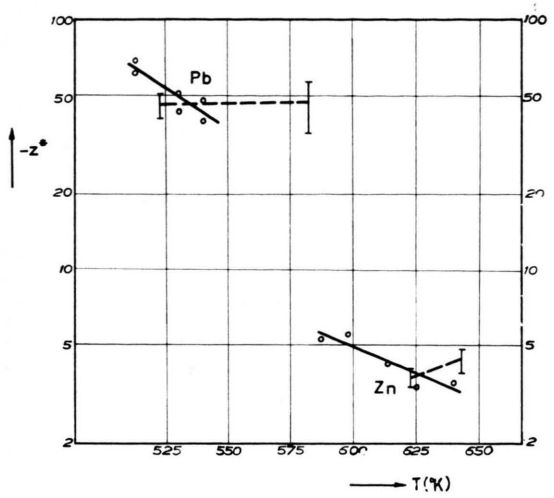

Fig. 2. Effective valence of diffusing Zn and Pb atoms as function of temperature. Definition according to Eq. (1) in text. Dashed lines and error margins: from ref. [6].

HUNTINGTON [2] (cf. a similar expression derived by one of the present authors [9] for isotope electrotransport),

$$z^*/z = [q^*/q - \tfrac{1}{2}(m^*/|m^*|)\,(\varrho^*/\bar{\varrho})]\,. \qquad (2)$$

Here q, q^* denote the ionization of an average, resp. a diffusing atom, $\bar{\varrho}$ is the specific resistivity of the metal, m^* the effective electronic mass. Although the formula takes into account the possibility of hole conduction, one should expect it to apply quantitatively only for electron conductors, as momentum transfer from defect charge carriers presents complicated aspects.

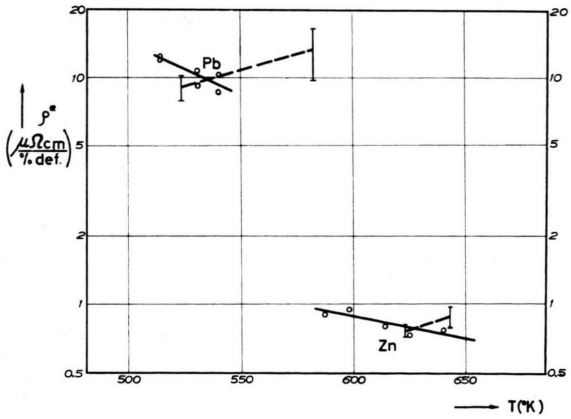

Fig. 3. "Effective defect resistivity" of Zn and Pb as function of temperature. Calculated via Eq. (2) in text, assuming $z_{Zn}=2$, $z_{Pb}=4$, $q^*=q$, $m^*=|m^*|$. Dashed lines and error margins: from ref. [6].

The "effective resistivities" shown in Fig. 3 have been calculated on the arbitrary assumptions that z is 2 for Zn and 4 for Pb, that $q^*/q=1$ (reasonable for self-transport), and that free electron approximation applies. The physical meaning of ϱ^* is with these simplifications naturally somewhat uncertain, but the object of the calculations leading to Fig. 3 has been to shed light on the question whether or not in an equation of the form

$$z^*\,e = (q^* - K/\bar{\varrho})\,, \qquad (3)$$

the factor K can be considered to be a constant, which is of importance e. g. if the true charge of an alloying element is to be determined by electromigration (plotting $z^*\,e$ vs. $\bar{\varrho}^{-1}$ gives q^* as intercept on $z^*\,e$ axis). The present results as well as those of practically all other non-isothermal measurements (see summary, ref. [5]) suggest that K diminishes as temperature rises. The sole exception is the investigation on In [5] where K was constant. The results of ref. [6], on the other hand, show an increase of K with temperature, although the wide limits of error allow the possibility of constancy or a slow decrease. Recent exact isothermal measurements on Au [8] gave constant K. The possibility cannot therefore be excluded that, while the reproducibility of the present result appears considerably superior to that of isothermal work on Zn and Pb, the observed decrease in K may be due to an inherent error liable to affect the non-isothermal method as such. No definite conclusions have been drawn as yet concerning the possible source of such an error. However, the recent discovery of microvoids in the cathode portions of In [5] and Ag [10] electromigration specimens may have a bearing on the problem. For In, a correction was actually introduced to cover this effect. In the present work, Zn exhibited a trace of microvoids, but not sufficiently clearly to warrant a safe correction. In Pb, metallographic examination was too difficult to give a reliable indication.

By conducting similar experiments using AC, a search was made for a thermotransport effect in Zn and Pb; from the observed marker motion, the SORET heats of transport Q^* were calculated (see ref. [11]). The results were $Q^*_{Zn} = (-0.2 \pm 1.5)$ kcal/mole, and $Q^*_{Pb} = (+2.1 \pm 4.0)$ kcal/mole. Thus no certain indication of thermotransport could be obtained in these metals. In Zn the small value of Q^* agrees with earlier measurements [12]. In Pb (where no earlier results are available) an accuracy limiting factor was that a substantial part of the AC effect may have been masked by the sagging of the specimen and by creep (see ref. [5]).

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