

## Ionic conductivity and anion diffusion in single crystals of lead chloride

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**Abstract.** The ionic conductivity and self-diffusion of chlorine ions in undoped single crystals of zone-refined lead chloride have been measured over the temperature range 625–370 K. These measurements suggest that the conductivity and self-diffusion are due to simple vacancy migration as confirmed by the observed correlation factor. The activation energy of formation of vacancies is found to be 1.55 eV and that for migration of an anion is 0.38 eV. In the extrinsic region, the two measurements show marked discrepancies which are explained by assuming the presence of oxygen impurity ions in the lattice, and the mechanisms for their contribution to the observed excess conductivity are discussed.

**Keywords.** Lead chloride; anion diffusion; ionic conductivity; transport property.

### 1. Introduction

It is known that the dominant lattice defect responsible for the ionic conductivity in pure and doped lead chloride is the anion vacancy (Jost 1952). The activation energy for migration of the anion vacancy has been measured by Simkovich (1963), Seith (De Vries 1965) and Gylai (De Vries 1965) in powder samples and is found to range from 0.48 eV to 0.24 eV. The measurements on single crystals of pure and doped lead chloride, however, show that the energy of formation of vacancies is 1.66 eV and that for migration of the anion vacancies is 0.35 eV (De Vries and Van Santen 1963; De Vries 1965).

The roles of various point defects in this material are not yet clearly understood. Simkovich, for example, concluded that in the extrinsic region half of the anion vacancies are associated with cation vacancies to form charged pairs. Barsis and Taylor (1966), on the other hand, proposed that appreciable number of interstitials, *i.e.*, unassociated Frenkel defects, are present in the extrinsic region as seen from the analysis of isotherms obtained by them from the data of De Vries and Van Santen. The recent experiments by Van den Brom *et al* (1972) on the dielectric relaxation in pure lead chloride suggest that in this region dipole species such as anion vacancy-impurity associates are present.

In this paper, we shall present the results of self-diffusion and ionic conductivity measurements made on pure crystals of lead chloride, and show that in this material Schottky defects are mainly responsible for the observed ionic transport and that the impurity anion vacancy associates, particularly the oxygen ions, influence it markedly in the extrinsic region.

## 2. Experimental

### 2.1. Material preparation

The preparation of high purity lead chloride by the conventional method of double decomposition of lead nitrate and hydrochloric acid poses special problems due to the marked tendency of lead chloride to form the hydroxychloride of lead. The equilibrium concentration of this compound in materials obtained by this method is sufficient to affect adversely the quality of single crystals grown from such a material. We have, therefore, purified the base material, which was prepared from Analar quality  $\text{Pb}(\text{NO}_3)_2$  and  $\text{HCl}$ , by treating it with gaseous chlorine at a temperature well above its melting point. This method, although effective to some extent, is very slow; hence, in order to purify it further, the material was zone-refined in a chlorine atmosphere before crystal growing. The zone-refined material was grown into single crystals again in a chlorine atmosphere from melt by the Stockbarger-Bridgman method in a quartz crucible. The samples were cleaved perpendicular to the *c*-axis from these ingots. The material with  $^{36}\text{Cl}$  doping was prepared by adding an appropriate quantity of  $\text{H}^{36}\text{Cl}$  at the time of double decomposition of lead nitrate to lead chloride. The methods of purification and crystal growth described earlier were employed to obtain samples for the tracer diffusion measurements. The typical specific activity of these samples was about  $100 \mu\text{Ci}$  per cubic centimeter.

### 2.2. Tracer diffusion measurements

Diffusion measurements were made using the isotope exchange technique previously described by Harrison *et al* (1959) and used extensively by Barr and Dawson (1967) for the study of anion diffusion in alkali halides. Our experimental arrangement (Viswanathan and Patankar 1972) is similar to that used by them except that we have replaced the proportional counter by a thin walled GM counter surrounded by an anti-coincidence counter cage. This modification was found not to affect the accuracy of our measurements, since the anion diffusion in lead chloride is many orders of magnitude faster than in the alkali halides. The specific activity of the samples was measured by using the method described by Harrison *et al* (1959) in which a known quantity of lead chloride obtained by powdering a piece from the single crystal was converted to dry  $\text{HCl}$  gas after letting it react with concentrated sulphuric acid. The activity present in the gas is related to the specific activity of the crystal samples used for diffusion measurements and was measured in the counting system with which isotope exchange of the samples was measured.

### 2.3. Conductivity measurements

The specimens used for diffusion measurements were subsequently employed for conductivity measurements. The conductivity of these samples was also measured before being used for diffusion experiments. All samples were annealed in chlorine atmosphere for several hours before measurements.

The specimens were 2–5 mm thick and had electrical contact areas of about  $1\text{--}2 \text{ cm}^2$ . Their surfaces in contact with the electrodes were ground, polished and first coated with an evaporated film of graphite about 2 microns thick. They were then covered with a thin layer of graphite paint. By this technique we could

avoid air gaps between the crystal and the electrodes and could provide even and durable electrical contacts. All measurements were made in chlorine atmosphere to avoid thermal decomposition at elevated temperatures. It was preferred to an inert atmosphere because it makes comparison of the conductivity measurements with those of diffusion valid, since in the latter we are dictated to use chlorine atmosphere because of the method we have chosen.

Conductance of the samples was measured with a Wayne-Kerr Autobalance bridge over a wide temperature range in a furnace whose temperature was controlled within  $\pm 0.1^\circ\text{C}$ . The measurements were made at a frequency of 1.5 kHz.

### 3. Results

Figure 1 shows a plot of  $\sigma T$  versus  $1/T$  obtained from the conductivity measurements made on a sample of lead chloride before and after the diffusion measurements. There is no marked difference, indicating that in the temperature range in which these measurements were made, impurity precipitation is to a large extent absent. The experimental observations of De Vries (1965) are also shown in the figure for comparison. Although there are slight discrepancies in the absolute values of  $\sigma T$  in these observations, the 'knee' which indicates transition between extrinsic and intrinsic conductivity regions is at 500 K, lower than that of De Vries' observations by about 50 K presumably due to high impurity content in his sample. The apparent activation energy for migration given by the slope of the curve in the extrinsic region is  $0.33 \pm 0.02$  eV, a value closer to that observed by these authors. Similarly, the energy of formation of the vacancies is found to be  $1.55 \pm 0.02$  eV, a value similar to those of De Vries (1965) and Hoshino *et al* (1969).

The conductivity measurements can be represented as diffusion coefficients by using Nernst-Einstein relation and the correlation factor  $f$  which depends upon

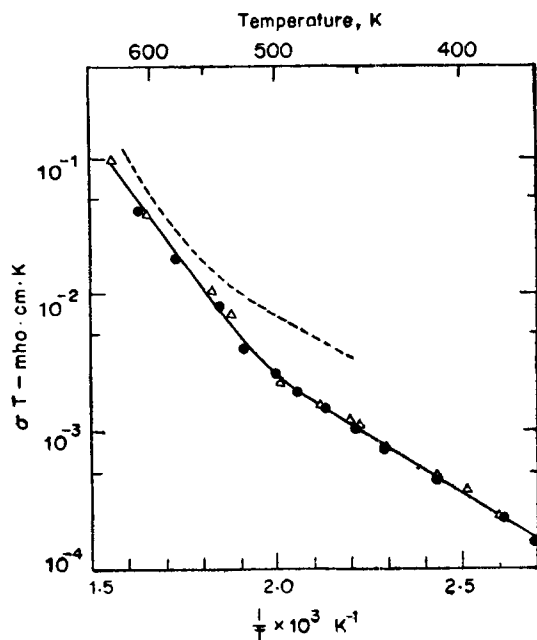


Figure 1.  $\sigma T$  vs  $1/T$  for pure lead chloride single crystal. ( $\Delta$ —before diffusion experiments and  $\bullet$ —after diffusion experiments), --- De Vries curve (De Vries 1965).

the crystal lattice as well as the mechanism of transport in the crystal (Lidiard 1957, Le Claire 1970, Friauf 1962). Figure 2 shows the diffusion coefficients obtained this way,  $D_{\sigma}$ , and the measured diffusion coefficients,  $D_{Cl}$ , over the temperature range of 625 K to 370 K.

In the intrinsic region both  $D_{\sigma}$  and  $D_{Cl}$  show similar dependence on temperature. The activation energy of formation of vacancies obtained from the least square fitting of the tracer diffusion data is found to be  $1.56 \pm 0.02$  eV, a value similar to that observed by Hoshino *et al* (1969) and De Vries (1965). Assuming that the contribution to diffusion from neutral defects, such as vacancy triplets and impurity-vacancy complexes, is negligible compared to that of the free anion vacancies in this temperature region, we can estimate the value of the correlation factor for this material. Our experimental results give for  $D_{Cl}$  the expression

$$D_{Cl} = 1.03 \times 10^{-3} \exp [(-0.79 \pm 0.03) \text{ eV}/kT] \text{ cm}^2 \text{ sec}^{-1}$$

and for  $D_{\sigma}$  from the intrinsic conductivity of these crystals we obtain

$$D_{\sigma} = 1.33 \times 10^{-3} \exp [(-0.78 \pm 0.01) \text{ eV}/kT] \text{ cm}^2 \text{ sec}^{-1}$$

giving for the correlation factor  $f$  as 0.77. The anion sublattice of lead chloride consists of a distorted hexagonal packing (Wyckoff 1963). The theoretical value of  $f$  for diffusion of free vacancies in the hexagonal close-packed structure is 0.78146 (Campaan and Haven 1956). The measured value of  $f = 0.77$  suggests that in lead chloride the anion transport to a large extent takes place through the vacancy jump mechanism.

In the extrinsic region the apparent activation energy for migration  $E_m$  obtained from the diffusion measurements is found to be  $0.38 \pm 0.02$  eV, a value slightly higher than that observed in our conductivity measurements.

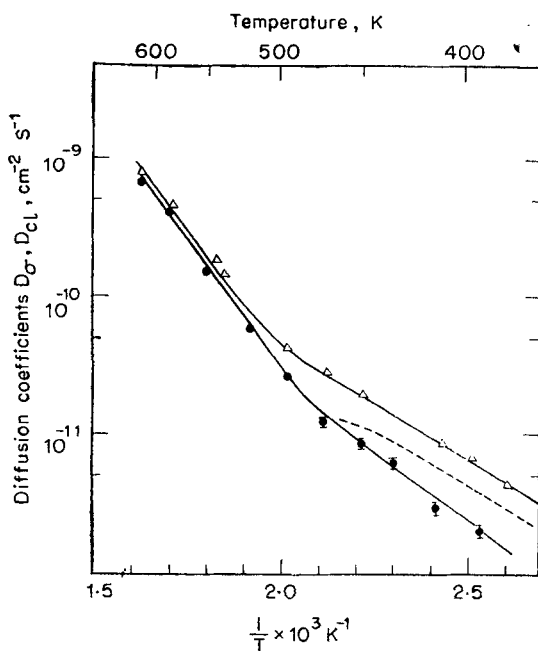


Figure 2.  $D_{\sigma}$  and  $D_{Cl}$  vs  $1/T$  for pure lead chloride. [ $\Delta$  -  $D_{\sigma}$  from Nernst-Einstein relation,  $\bullet$  -  $D_{Cl}$  from isotope exchange experiments, - - - ( $D_{\sigma} - D_{Cl}$ ) curve].

Another interesting feature of these measurements in this region is that the Nernst-Einstein relation is not strictly verified. Similar discrepancies were observed by Beniere *et al* (1971) in the case of the cation diffusion in NaCl and were accounted for by assuming the presence of highly associative complexes of impurity and vacancies which contributed to the observed diffusion. In pure lead chloride the diffusion coefficients  $D_{\sigma}$  are about a factor of two larger than the values of the corresponding  $D_{\text{cl}}$  over the temperature range of 490 K to 370 K. In figure 2,  $(D_{\sigma} - D_{\text{cl}})$  is shown in this temperature region. Assuming this curve to be exponential in the first approximation, we get the activation energy of 0.31 eV. Schoonman (1970) has observed increased conductivity in the case of lead bromide when measurements were made in bromine atmosphere at varying pressures. We have not observed any substantial variation in the conductivity of our samples as a function of chlorine pressures.

#### 4. Discussion

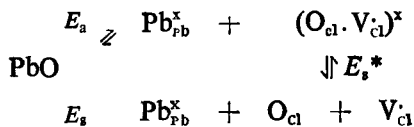
The experimental results outlined in the preceding sections lead us to conclude that in the temperature range of 625 K to 370 K anionic transport is predominantly responsible for the observed diffusion and conductivity, and it takes place primarily through a simple vacancy migration. In the intrinsic region, the conductivity, and diffusion measurements give values for the sum of enthalpy of motion and that required to produce a defect, which are in agreement with other authors. In spite of the fact that the conductivity was measured along *c*-axis and the diffusion was measured in all the three crystallographic axes, the agreement between these measurements suggest that within the experimental accuracies the activation energies are isotropic as observed by De Vries. The occurrence of interstitials in this material, suggested by Barsis and Taylor (1966), appears to be less likely. The mechanism by which holes are generated at the surface in the presence of chlorine atmosphere, similar to that suggested by Schoonman for the observed bromine-pressure-dependent conductivity of lead bromide, is not observable. This can be explained on the basis of the observations made by Wajszel (1963) on the formation of lead chloride on lead layers exposed to chlorine at 300 K. The transport number for holes calculated from his observations is  $1.1 \times 10^{-4}$ , a value about two orders of magnitude smaller than that for lead bromide (Schoonman 1973).

In the extrinsic region, where impurities are expected to influence the transport properties of the crystal, our conductivity and diffusion data do not obey the Nernst-Einstein relation, indicating association of the anion vacancies with charged impurities. It seems that these are totally dissolved above 490 K. Moreover, both the constituents of the associates are mobile and contribute to the conductivity giving values almost twice as high as those expected from 'vacancy only' conduction. If we limit ourselves to neutral complexes only for reasons of charge compensation, we are left with two possible candidates: a cation vacancy and two anion vacancies forming a neutral vacancy triplet, and a substitutional doubly negatively charged impurity ion associating with an anion vacancy. The neutral vacancy triplets appear to be less likely because the association energy required for this configuration, as calculated by De Vries (1965) on the coulombic model, is about 1.03 eV, much higher than the value obtained from our experiments. In addition, the concentration of the cationic impurities is too low to produce

appreciable concentrations of cation vacancies at such low temperatures for the formation of these triplets. On the other hand, a majority of anion vacancies responsible for the observed transport may be produced to attain equilibrium with the divalent anionic impurities present in the material, and form associates with them. Hence, in relation to the impurity associates, the contribution of the vacancy triplets is expected to be negligible, and we would consider only the role of these associates for further discussion.

The major impurity present in our material before refinement was oxygen introduced due to our method of preparing the base material. Although the pre-zone refinement treatment and the subsequent zone refinement are meant to remove a large proportion of this inherent oxygen, it is expected that our samples contain an appreciable amount of it so as to influence our measurements in the extrinsic region. Van den Brom, Schoonman and De Wit (1972) have shown the presence of associates of oxygen and anion vacancies in  $\text{PbCl}_2$  and  $\text{PbBr}_2$  by measuring their dielectric losses. They conclude from their observations that the degree of association between them is very high; as a result, their pure samples which were prepared in a manner similar to ours had oxygen impurity content almost fifty times that of other dopants naturally present. Unfortunately, we are not in a position to relate our observations with the actual concentration of oxygen in our samples, since an accurate analysis for oxygen is still lacking. We shall therefore confine to qualitative discussion of the possible effects of oxygen on the conductivity and diffusion in the light of our observations.

Incorporation of oxygen from oxide precipitates in lead chloride will lead to the following lattice reaction expressed in Kröger's notation:



where  $E_a$ ,  $E_s$  and  $E_s^*$  are the enthalpies of association, dissociation, and dissolution to unassociated defects respectively. They are interrelated in such a way that  $E_s^* + E_a = E_s$ . In addition, there can be an association reaction, typical of a substitutional oxygen atom, in which the local charge neutrality at the site is achieved by an associated hole, probably shared by the neighbouring lead ions of the lattice.

Our conductivity measurements do not distinguishingly show the stages of association and dissociation over the measured extrinsic range, indicating that we are essentially dealing with a system having low association energy. Moreover, the values of  $D_\sigma$  are almost three times that of  $D_{\text{Cl}}$ , strongly suggesting presence of charge carriers other than the anion vacancies which alone are responsible for the observed diffusion. In the following discussion, we shall examine these two possible sources of additional charges in the light of our observations.

The incorporated oxygen, if associated with an anion vacancy, will contribute to the diffusion by releasing the anion vacancy but its contribution to the conductivity is possible only if it can migrate in the lattice. The doubly charged oxygen

ion has smaller ionic radius ( $1.32 \text{ \AA}$ ) compared to that of the chlorine ion ( $1.81 \text{ \AA}$ ), and is therefore likely to move either interstitially or by a jump in a neighbouring anion vacancy. Since the available interstitial space is only  $0.7 \text{ \AA}$ , much smaller compared to the ionic diameter of the oxygen, it appears that the transport in this case will take place only through substitutional jumps in the neighbouring sites. The observed factor of approximately two in the values of  $D_{\text{Cl}}$  and  $(D_{\sigma} - D_{\text{Cl}})$ , though coincidental, will be due to two electronic charges of the migrating oxygen ion, provided its mobility is nearly the same as that of the anion vacancy. The slope of  $\ln(D_{\sigma} - D_{\text{Cl}})$  versus  $1/T$  plot will in that case give the sum of the enthalpy of motion and a half of the energy of association for the oxygen ion, the other half being shared by the dissociated anion vacancy.  $E_a$  can be deduced from the experimentally observed activation energy and the enthalpy of motion for the anion vacancy. The enthalpy of motion obtained by other authors from their studies of doped single crystals of lead chloride varies from  $0.20 \text{ eV}$  (Hoshino *et al* 1969) to  $0.35 \text{ eV}$  (De Vries 1965).  $E_a$  will therefore take values between  $0.36 \text{ eV}$  and  $0.06 \text{ eV}$  and the corresponding values of the enthalpy of motion for oxygen impurity ions would be between  $0.13 \text{ eV}$  and  $0.28 \text{ eV}$ . We are more inclined to accept the association energy of  $0.06 \text{ eV}$  because Hoshino *et al* do not take into consideration the effects of association in their analysis.

The second possible charge carriers mentioned earlier are the holes shared by the lead ion neighbouring the oxygen ion frozen in the lattice. De Vries (1965) had attempted to measure the Hall mobility of these holes assuming that the holes will give lead chloride p-type conductivity. He could not measure any detectable Hall conduction in the samples doped with oxygen. This is expected if the hole is not free but associated with lead ions giving chemically stable charged state  $\text{Pb}^{3+}$  at the site. On heating the sample the hole will move from the oxygen ion to a neighbouring one by hopping process thus contributing to the conductivity with an activation energy of  $0.31 \text{ eV}$  as given by the  $(D_{\sigma} - D_{\text{Cl}})$  plot. The  $\text{Pb}^{3+}$  ion formed due to localisation of hole is in S state ion; however, the recent experiments of De Vries (1973) on the ESR of these ions in oxygen doped lead chloride has not shown any paramagnetic resonance absorption, suggesting that the system is subjected to fast relaxation processes such as rapid jumps by the holes. The available evidence is obviously not in favour of this mechanism. Nevertheless, it is an interesting possibility needing closer examination by other experimental techniques.

## 5. Conclusions

The simultaneous measurements of the ionic conductivity and diffusion in undoped lead chloride have shown that the anions are responsible for the observed conductivity and diffusion. Oxygen has strong tendency to associate itself in the lattice and to influence the conductivity by providing additional charge carriers in the extrinsic region.

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### References

- Barr L W and Dawson K 1967 *Proc. Brit. Ceram. Soc.* **9** 171  
Barsis E and Taylor A 1966 *J. Chem. Phys.* **45** 1154  
Beniere F, Beniere M and Chemla M 1971 *Z. Naturforsch.* **26** 915  
Campaan K and Haven Y 1956 *Trans. Faraday Soc.* **52** 786  
Dawson K 1968 Thesis, Reading University, Reading.  
De Vries K J 1965 Thesis, University of Utrecht, Utrecht.  
De Vries K J and Van Santen S J 1963 *Physica (Utrecht)* **29** 482  
Friauf R J 1962 *J. Appl. Phys.* **33** 494  
Harrison J A, Hoodless I M and Morrison L G 1959 *Discus. Faraday Soc.* **28** 103  
Hoshino H, Yamazaki M, Nakamura Y and Shimoji M 1969 *J. Phys. Soc. Japan* **26** 1422  
Jost W 1952 *Diffusion* (Academic Press Inc., New York) p.204  
Le Clair A D 1970 *Correlation effects in diffusion in solids*, in "Physical Chemistry—An Advanced Treatise," Vol. X (Academic Press Inc., New York) pp.261-330  
Lidiard A B 1957 *Handbuch der Physik*, Vol. **20** (Springer-Verlag, Berlin) pp.246-349  
Schoonman J 1970 *J. Solid State Chem.* **2** 31  
Schoonman J 1973 Private communication.  
Simkovich G 1963 *J. Phys. Chem. Solids* **24** 213  
Van den Brom W E, Schoonman J and De Wit J H W *J. Solid State Chem.* **4** 475  
Vishwanathan K and Patankar A V 1972 *Proc. Nucl. Phys. Solid State Phys. Symp. (India)* **14C** 177  
Wajszel D 1963 *J. Electrochem. Soc.* **110** 504  
Wyckoff R W G 1963 *Crystal structure* Vol. **1** (Interscience Publishers Inc., New York), p. 298