

## Point Defects in Potassium Thiocyanate: Impurity Diffusion and Conduction in Lead-Doped Crystals

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Received July 24, 1973

The diffusion rates of  $^{210}\text{Pb}^{2+}$  and  $^{35}\text{S}^{2-}$  into single crystals of nominally pure potassium thiocyanate have been measured. The impurity diffusion coefficients are about 1% of the values for the host anion and cation (reported previously), and this supports the view that ionic diffusion in this solid occurs mainly via a vacancy pair process. The electrical conductivity of polycrystalline samples of KSCN doped with  $\text{Pb}^{2+}$  has been measured as a function of temperature and of lead content. The results show that cation vacancies are mobile in the solid and that the overall conduction behavior of KSCN is dominated by impurity effects.

### Introduction

The current interest in the use of solid ionic conductors in various devices has increased the desirability of finding solid electrolytes with a high ionic mobility. Many of the solids which already have this property, e.g.,  $\text{AgI}$ ,  $\text{Ag}_4\text{RbI}_5$ ,  $\text{Li}_2\text{SO}_4$  (1), owe their high conductivity to the existence of a disordered structural modification, which results in an order-disorder transition in the solid below the melting point. The overall ionic conductivity of a solid is a function not only of ionic mobility, but also of the concentration of point defects in the lattice. This latter quantity determines the number of ions (or defects) which can move in the solid, and is itself determined by the Gibbs free energy of formation of the defects. This is expressed by the well-known equation:

$$\begin{aligned} x_a \cdot x_b &= \exp(-g_f/kT) \\ &= (\exp - S_f/k)(\exp - h_f/kT), \end{aligned} \quad (1)$$

where  $x_a$  and  $x_b$  are the mole fractions of the two complimentary point defects (a Schottky or Frenkel pair), and  $g_f$ ,  $h_f$ , and  $s_f$  are the Gibbs free energy, enthalpy, and entropy of formation of the pair, respectively. The theory describing

the interaction and motion of these point defects in a solid has been well established and is thoroughly described elsewhere (2). The thermodynamic parameters relating to defect formation may be expected to correlate with other physical properties of the solid, e.g., melting temperature and Debye characteristic temperature. In particular, Barr and Lidiard (3) have summarized the correlation between  $h_f$  for Schottky defects and the melting temperature ( $T_m$ ) of halides by an empirical relationship

$$h_f = 2.14 \times 10^{-3} T_m, \quad (2)$$

with  $h_f$  in electron volts and  $T_m$  in degrees Kelvin.

Insufficient information exists in the literature to enable this type of correlation to be extended to other groups of ionic crystals, but, in general, it is reasonable to assume that the lower the melting temperature, the easier it will be to form whatever type of point defect is intrinsic to a particular crystal.

Based on the above, we have considered that low-melting ionic solids should be able to satisfy at least some of the criteria required for high conductivity. Yet, in spite of this, no example of such a solid stands out as a good conductor (although experimental studies are few), and, hence, it seems apparent that mass transport in these materials is largely dependent on defect

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interaction and other factors besides concentration.

A preliminary investigation into this problem has been made with potassium thiocyanate ( $T_m = 448^\circ\text{K}$ ), and this work has shown that KSCN is a very poor conductor at temperatures up to its melting point, and that its defect behavior appears to be more consistent with a molecular-type crystal than a true ionic solid.

In a previous publication (4), we discussed some aspects of the defect behavior of KSCN, based on conduction and diffusion measurements in nominally pure single crystals. This work showed a large deviation from the Einstein relation in the sense that the observed ionic diffusion was much greater than that calculated from the measured ionic conductivity. It was also found that the anion and cation diffusion coefficients in the crystal were essentially equal, from which it was concluded that diffusion in KSCN occurs predominately by a vacancy pair mechanism. In this present paper we give further support to this conclusion from measurements of the diffusion of  $\text{Pb}^{2+}$  and  $\text{S}^{2-}$  into crystals of pure KSCN. The application of the simple theory of ionic conductivity to our previous results yielded a value of 3.23 eV for  $h_f$ , the enthalpy of formation of the defect in KSCN. This value is anomalously high when compared with the values for other simple ionic crystals, and raises the question of whether the conduction in the high temperature region is a true intrinsic conduction, or whether it is influenced by the crystallographic transition in the solid at  $414^\circ\text{K}$ . Further discussion of this question is now possible from the results of ionic conduction and heat capacity studies in  $\text{Pb}^{2+}$ -doped KSCN which are presented in this paper. Our results are also discussed in comparison with recent conduction measurements by Chadwick et al. (5).

## Experimental

The method of measurement of the AC conductance was as previously described (4). Attempts to grow good single crystals of the lead-doped KSCN were unsuccessful and so all the conductance data refer to polycrystalline material. However, previous work had shown that there was very little difference between the conductance of a single crystal and a polycrystalline sample of the same purity. The doped samples were prepared by melting together

weighed amounts of the two components. Experiments showed that  $\text{Pb}(\text{SCN})_2$  was soluble in molten and solid KSCN in the concentration ranges studied. After a set of measurements was completed, the analysis of each sample was confirmed by determination of the lead content by atomic absorption.

All diffusion measurements were made on single crystals of zone-refined KSCN. The diffusion of  $\text{Pb}^{2+}$  was measured by vacuum deposition of  $^{210}\text{PbCl}_2$  on one crystal surface, followed by the conventional microtome sectioning technique. The activity of the lead was determined with a Nuclear Enterprise  $\gamma$ -ray spectrometer using a well-type sodium iodide scintillation head. Diffusion coefficients were obtained from the penetration profiles using the solution to Fick's Law for a semi-infinite solid. Some measurements of the diffusion coefficient for  $\text{S}^{2-}$  were also obtained in this way, using  $\text{Na}_2^{35}\text{S}$ , but the majority of the sulphide diffusion results were obtained using the surface decrease method in which only the surface activity of the crystal is measured before and after the diffusion anneal. In this method the diffusion coefficient  $D$  is obtained from the equation (6)

$$n^*_t/n^*_{(t=0)} = \exp(\mu^2 Dt) [1 - \text{erf}(\mu^2 Dt)^{1/2}], \quad (3)$$

where  $n^*_{(t=0)}$  and  $n^*_t$  are the surface activities before and after annealing for time  $t$ , respectively, and  $\mu$  is the absorption coefficient for the radiation in the sample. The latter quantity was obtained experimentally using aluminium absorbers and converted to the absorption coefficient for KSCN using the density of the thiocyanate. This procedure was necessary since it was not possible to prepare very thin absorbing discs of KSCN. The result obtained was

$$(\mu)_{\text{KSCN}} = 435.7 \text{ cm}^{-1}.$$

The heat capacities of pure and doped KSCN were measured with a Perkin-Elmer Differential Scanning Calorimeter DSC 1B.

## Experimental Results and Discussion

### Impurity Diffusion

Any "excess" in the observed ionic diffusion over that calculated from the ionic conduction via the Nernst-Einstein equation after taking proper account of correlation effects, is customarily attributed to the existence of neutral defects

TABLE I  
IMPURITY DIFFUSION IN KSCN

$T$ (°C)	$D$ $^{210}\text{Pb}^{2+}$ ( $\text{cm}^2 \text{sec}^{-1}$ )	$T$ (°C)	$D$ $^{35}\text{S}^{2-}$ ( $\text{cm}^2 \text{sec}^{-1}$ )
116.0	$9.8 \times 10^{-12}$	72.0	$1.64 \times 10^{-12}$
142.0	$5.3 \times 10^{-11}$	90.3	$3.59 \times 10^{-12}$
		108.5	$1.04 \times 10^{-11}$
		124.0	$2.08 \times 10^{-11}$

which contribute to diffusion but not to conduction. The existence of an important contribution from anion-cation vacancy pairs has already been inferred in our previous work from a comparison of the  $^{42}\text{K}^+$  and  $\text{S}^{14}\text{CN}^-$  diffusion coefficients, but the "excess" diffusion may also contain contributions from neutral complexes between the cation vacancy and an impurity cation, and also between an anion vacancy and an impurity anion. The existence of these impurity complexes and their contribution to the

overall diffusion can be established from the diffusion coefficients of an aliovalent anion and an aliovalent cation in the crystal. The diffusion coefficients of  $^{210}\text{Pb}^{2+}$  and  $^{35}\text{S}^{2-}$  are given in Table I, and are shown plotted against reciprocal temperature in Fig. 1. The host anion and cation diffusion coefficients are also shown in Fig. 1 for comparison.

In making the measurements of Table I, it has been assumed that lead and sulphur go into the lattice of KSCN as  $\text{Pb}^{2+}$  and  $\text{S}^{2-}$ , respectively. The ready solubility of  $\text{Pb}(\text{SCN})_2$  in KSCN, and the similarity of ionic radii of  $\text{Pb}^{2+}$  and  $\text{K}^+$  (1.20 Å and 1.33 Å), support this assumption in the case of lead, although no direct experimental evidence of the state of either impurity species has been obtained.

It is seen that the diffusion rate for both types of impurity is about two orders of magnitude less than that of the host ions. In fact, because of the very slow diffusion of  $\text{Pb}^{2+}$ , it was difficult to obtain good sectioning profiles, and so these results must be regarded as giving only an approximate value of the activation energy of diffusion. It is recognized that these measurements do not give any information about the mechanism of impurity diffusion, and take no account of the influence of grain boundaries, but the effect of the latter would most likely be to enhance the diffusion rate. The results show that impurity-vacancy complexes do not make an appreciable contribution to the total ionic diffusion and that the observed deviation from the Nernst-Einstein equation may reasonably be attributed to host-anion-cation vacancy pairs.

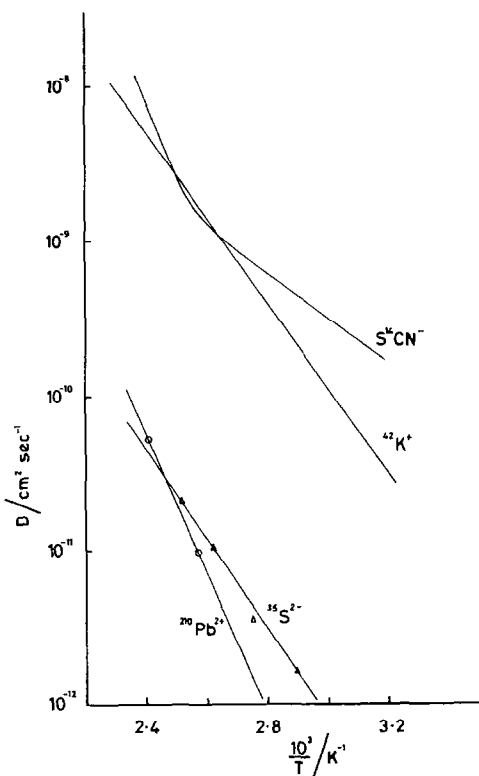


FIG. 1. Tracer diffusion coefficients in KSCN.

#### Electrical Conduction in KSCN Doped with Lead Cations

The conductivity plots for pure KSCN reported previously showed a well-defined break into two regions similar to the extrinsic and intrinsic behavior observed in alkali halides, and a corresponding assignment of the two regions for KSCN seemed reasonable. These results gave values of 0.59 eV for  $h_m$ , the enthalpy of migration of the mobile defect, and 3.23 eV for  $h_f$ , the enthalpy of formation of an isolated defect pair. This value of  $h_m$  is comparable to the values obtained for alkali halides (0.71 eV for KCl, 0.65 eV for KBr), but the value of  $h_f$  is considered to be anomalously high, particularly in view of the low melting temperature. Tilley (7) and Chadwick et al. (5) have summarized the reported

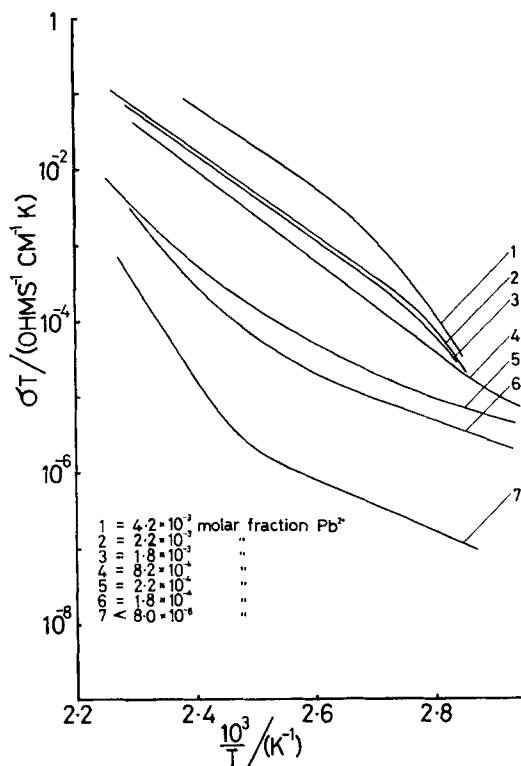


FIG. 2. Conductance of lead-doped KSCN.

conductance results for KSCN, and in no case is there any evidence of a high temperature activation energy which could be commensurate with a low value of  $h_f$ . Attention was first drawn to the high value of  $h_f$  by Plester et al. (8) whose conductance results gave a value of 3.53 eV. Potassium thiocyanate has a well-documented transition in the solid at 414°K (9), above which the  $\text{SCN}^-$  ions are randomly distributed with respect to the two alternative orientations in the 001 planes. The temperature of the transition is close to that of the "knee" in the conductance curves and if the electrical behavior in the high temperature region is influenced by the transition, then clearly the application of the simple theory of conductance to the two portions of the plot would be unjustified. We have not observed any appreciable discontinuity in conductance of the pure material at the transition point, in contrast to the findings of Chadwick et al. (5). The crystal structures of the high- and low-temperature modifications of KSCN are virtually the same, and if the transition does not affect the mobile species in the conduc-

tion process, then a marked change in conduction at the transition would not be expected. The effects of transitions upon conduction when these considerations do not hold are well known in  $\text{KHF}_2$  (10) and  $\text{CsCl}$  (11, 12). Our experimental results for the conductance of KSCN containing various amounts of  $\text{Pb}^{2+}$  are shown in Fig. 2. It is evident that the conduction is enhanced by addition of the impurity cation, down to the lowest concentrations studied. At lower temperatures, there is a linear relationship between conductance and  $\text{Pb}^{2+}$  content (Fig. 3), indicating that in this region the conduction is due to the movement of cation vacancies. Figure 2 also shows that the conduction of doped KSCN increases with  $\text{Pb}^{2+}$  content in a fairly uniform way throughout the temperature range studied and the results show no evidence, even at low  $\text{Pb}^{2+}$  content, of merging into a common linear plot at high temperatures, which could then be reasonably attributed to intrinsic behavior. This indicates that thermally produced defects do not dominate the conduction behavior of KSCN until a much higher relative temperature is reached than is customarily found with other ionic salts. Because of this, it is doubtful if any

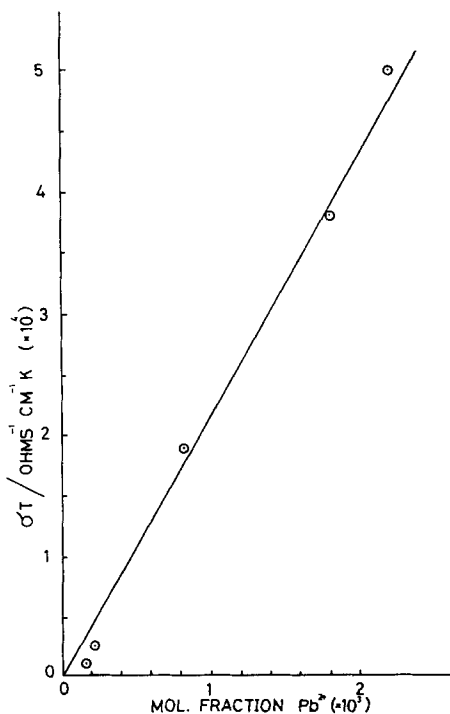


FIG. 3. Conductance of KSCN as a function of lead content (at 100°C).

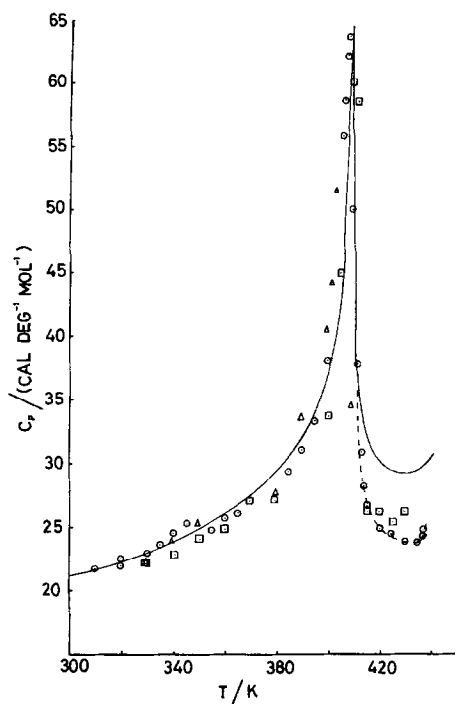


FIG. 4. The heat capacity of pure and lead-doped KSCN.  $\circ$ , zone refined;  $\Delta$ , containing 0.01%  $\text{Pb}^{2+}$ ;  $\square$ , containing 1.65%  $\text{Pb}^{2+}$ ; (—), Sakiyama *et al.* (9).

portion of the conduction plot can be unambiguously ascribed to the formation of point defects, even with samples of quite high purity. Chadwick *et al.* (5) have analyzed their conductance curves to obtain values of  $h_f$  and  $h_m$  for each of the two solid modifications, but in view of the foregoing observations on doped materials, such a procedure does not seem justified. The change in slope which is observed in the conduction plot for "pure" KSCN is not a direct and necessary consequence of the thermal transition as can be seen by comparison of Figs. 2 and 4. In Fig. 4, the heat capacity of the solid shows a well-defined lambda transition for both the pure and  $\text{Pb}^{2+}$ -doped materials, while the conductance plots for similarly doped solids (Fig. 2) show no change in slope. Our heat capacity measurements for the pure material are in essential agreement with those of Sakiyama *et al.* (9).

Dreyfus and Nowick (12) have characterized four distinct regions in the conductivity curve of a doped material. Using their notation, the results in Fig. 2 may be interpreted as showing the impurity-controlled free vacancy region (II), and the impurity precipitation region (IV).

There is no distinct region that can be attributed to impurity association (III) and, hence, it is not possible from these results to derive quantitative information about association of  $\text{Pb}^{2+}$  cations with  $\text{K}^+$  vacancies. However, the absence of this region from the curves implies that the extent of association is very small and this agrees with the conclusions drawn from the  $^{210}\text{Pb}^{2+}$  diffusion.

In the correct evaluation of  $h_m$  from the conduction plots of doped samples, an essential requirement is that the slope of the free vacancy region must remain constant as the amount of dopant increases. This is well illustrated in the conduction of sodium chloride doped with  $\text{Sr}^{2+}$  (13), and with  $\text{Ba}^{2+}$  (14). For lead-doped KSCN, the slope of the graph between about 363°K and 400°K is found to increase from the value found for the "pure" solid (0.59 eV) to a constant value of 1.24 eV at about  $8 \times 10^{-4}$  mole fraction of  $\text{Pb}^{2+}$ . This value is taken here to represent the true enthalpy of migration of the cation vacancies introduced by the lead doping, and the lower activation energy observed in "purer" materials is presumed to be due to mobile anion impurities, the most likely of which are oxide or hydroxyl. A comparison of previous work shows that different authors agree reasonably well about the value of the high-temperature activation energy, but are most inconsistent about the low-temperature region. The present work shows that the shape of the conduction plot is extremely sensitive to the presence of trace impurities and that some previous assignments of the low activation energy to cation vacancy mobility are probably incorrect. Lomelin and Neubert (15) have commented on the effects of water on the low-temperature activation energy, and their value of 1.30 eV for  $h_m$  is in reasonable agreement with our present value obtained from the doped conductivity runs. Recently, Barr and Dawson (16) have shown how errors in the evaluation of  $h_f$  result directly from overestimation of  $h_m$ , but none of the existing measurements on KSCN give defect parameters which are even approximately consistent with its low melting temperature. A fair conclusion is that KSCN is a pseudo-ionic crystal, with transport behavior which reflects a "molecular" or ion-pair diffusion, and with electrical conduction dominated by trace impurities. In this respect KSCN resembles ice which also exhibits a large deviation from the Einstein equation with  $D_T > D_\sigma$  (17).

## Conclusions

The diffusion rates of  $\text{Pb}^{2+}$  and  $\text{S}^{2-}$  into single crystals of purified potassium thiocyanate are found to be much smaller than those of the host ions. It is concluded that neutral complexes formed between impurity ions with host ion vacancies do not contribute appreciably to the overall mass transport in the crystal. This is supported by the lack of any well-defined impurity association region in the conductance plots of lead-doped KSCN. These conclusions reinforce previous views that ionic diffusion in KSCN occurs predominately by a vacancy pair or "molecular" process. The conductance results for  $\text{Pb}^{2+}$ -doped potassium thiocyanate show that cation vacancies are mobile in the solid, and a value of 1.24 eV has been obtained for the enthalpy of migration to this defect. It is suggested that a lower value reported previously is probably due to mobile anion impurities. The overall shape of the conductivity curve for KSCN is shown to be much more sensitive to impurities than is usually found in, for example, alkali halides, and it seems unlikely that a true intrinsic ionic conductance is observed with samples which would otherwise be considered to have acceptable purity.

## Acknowledgment

The authors thank Dr. L. W. Barr for enlightening discussion.

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