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Tracer Diffusion Study of CuCl

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Diffusion coefficients for Cu^+ diffusion in γ- and β-phase CuCl have been measured with an *in situ* tracer diffusion technique. The diffusion coefficients were measured at five temperatures in the γ-phase and at two temperatures in the β-phase. The diffusion in the γ-phase was shown to follow an Arrhenius law with an activation energy of 1.4(1) eV. © 1992 Academic Press, Inc.

1. Introduction

The copper halides CuX (X = Cl, Br, I) form a series of isostructural compounds exhibiting several interesting properties such as sequences of structural phase transitions and fast ionic conductivity at elevated temperatures. All three compounds have the cubic zinc blende structure in their low-temperature γ-phases. Their β-phases are hexagonal and the fast ionic conducting α-phases are cubic. The structure of α-CuBr is closely related to the α-AgI structure in which the iodine ions form a body centered cubic lattice. It has been proposed that α-CuI has the zinc blende structure in which the iodine ions are arranged on a face centered cubic lattice (*1*). It has recently been shown, however, that Cu^+ ions in α-CuI are randomly distributed over all the tetrahedral sites (*2*). Only CuBr and CuI transform to the α-phase, while in the case of CuCl melting takes place before the structure transforms to the α-phase. The phase transition from the γ- to the β-phase takes place at 680 K in CuCl (*3*).

Cu^+ is a favorable ion for diffusion in the solid state because of its high polarizability. The series of anions Cl^-, Br^-, and I^- exhibit an increasing polarizability as well as decreasing electronegativity. The degree of covalency therefore increases along this series, and copper iodide would be expected to have the highest ionic conductivity for a given crystal structure. However, a comparison of measured conductivities shows that the ionic conductivity decreases by going from CuCl to CuI at the upper end of the temperature interval in which the γ-phases are stable (*4*). The total conductivity of CuCl contains an electronic contribution which is highly dependent on the stochiometry of the compound. It has been shown that the electronic conduction is of p-type, in Cu-

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deficient samples, and that the ionic conductivity dominates at high temperatures (*5*).

Measurements of diffusion coefficients are important for the understanding of the physical properties of fast ionic conductors. Therefore we have performed an *in situ* tracer diffusion study of γ- and β-phase CuCl. The radioactive Cu^+ tracer ions are in this method generated within a thin slice in the sample material itself by neutron irradiation. The values for the diffusion coefficients obtained from this study will be used for an evaluation of the usefulness of the interatomic pair potentials used for molecular dynamics simulations of the static and dynamic properties of this material. The aim of these studies is to study and compare the pair potentials of the copper halides in the solid phases as well as in the liquid state. CuI has been previously studied by an *in situ* tracer method as well as being simulated by molecular dynamics (*6*, *7*). Recently we have performed an additional *in situ* tracer diffusion study of the Cu^+ diffusion in β-phase CuI (*8*).

2. Experimental

The sample was prepared by adding anhydrous sodium sulfite to a stirred solution of $CuCl_2$ from which CuCl slowly precipitates. The precipitate was first washed with a dilute sulfurous acid solution, thereafter with glacial acetic acid, and finally with absolute alcohol. The sample was dried in an oven for 60 min at 90°C (*9*), transfered to a pyrex tube, heated to 120°C under vacuum for 3 hr and then melted under 0.3 atm of argon. The sample was cooled slowly to room temperature to avoid the formation of cracks. X-ray diffraction showed that the sample contained no impurity phases. No chemical analysis was done.

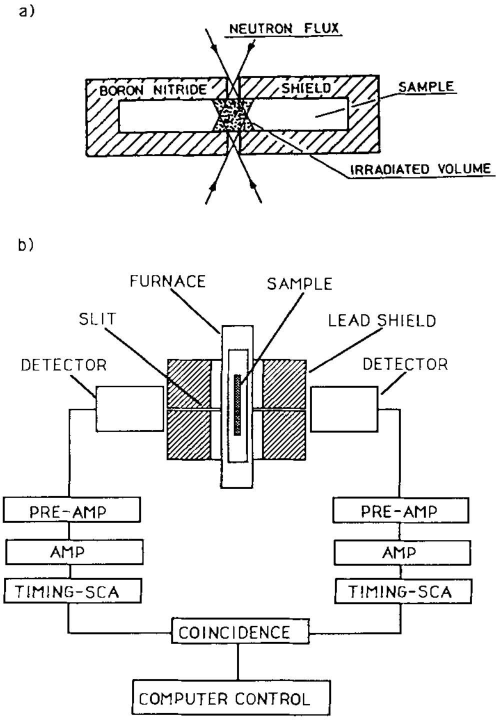

FIG. 1. (a) Container used for thermal neutron activation of the sample. (b) Schematic drawing of the experimental setup for the *in situ* tracer diffusion measurement. During the measurement the sample is moved upward past the slit in the lead shield. The two NaI detectors are counting the emitted gamma photons in coincidence.

The equipment used for the diffusion coefficient measurement is an improved version of the equipment used for the CuI measurement in Ref. (*7*). The irradiation of the sample was done in the R2 reactor at Studsvik, Sweden. The container used for irradiation is shown in Fig. 1a. Boron nitride is used as absorbing material and thermal neutrons can only penetrate into the sample through the Al ring at the middle of the can. A thin slice of radioactive ^{64}Cu tracer ions is in this way generated in the sample. ^{64}Cu has a half-life of 12.8 hr, and it decays by emission of a positron. The positron undergoes annihilation with an electron, and two gamma photons with energies 511 keV are emitted 180° apart. The experimental setup for the measurement of the activity profile is shown in Fig. 1b. The sample is located in a helium-filled copper tube which is mounted inside a vacuum furnace. The high thermal conductivity of the copper tube ensures a minimal thermal temperature gradient over the sample. The furnace is mounted on a vertical stepping motor controlled table. The stepping motor as well as the counting chain are interfaced to a personal computer, and activity profiles are automatically recorded as a function of time. Detectors and furnace are located inside lead shields, and the volume element in which the activity is measured is defined by a horizontal slit in the lead shield. The lead shield is constructed so that the resolution can be varied by changing the size of the slit. The photons emitted by the decaying ^{64}Cu nuclei are detected by two NaI detectors in coincidence. This method ensures that only photons originating from the tracer Cu ions are detected.

The spatial distribution of radioactive nuclies at t is related to the initial distribution at $t = 0$ though the equation

$$I(x,t) = e^{-\lambda t} \cdot \int I(x',0)P(x - x',t)dx', \quad (1)$$

where $I(x,0)$ is the distribution measured at $t = 0$, λ is the radioactive decay constant, and $P(x,t)$ is the diffusion function to be determined. In the present cylindrical geometry, the solution to the diffusion equation depends only on the coordinate x along the cylinder,

$$P(x,t) = \frac{S(0)}{2\sqrt{\pi Dt}} e^{-x^2/4Dt}, \quad (2)$$

where $S(0)$ is the total source strength at $t = 0$ and D is the diffusion coefficient. The activity profile is therefore at all times a function with variance

$$\sigma^2(I(x,t)) = \sigma^2(I(x,0)) + \sigma^2(P(x,t)). \quad (3)$$

From Eq. (1) it is seen that $\sigma^2(P(x,t)) = 2Dt$, and D is therefore determined directly from the variance of the measured activity profile by the equation

$$D = \frac{1}{2t}\{\sigma^2(I(x,t)) - \sigma^2(I(x,0))\}. \quad (4)$$

When mounted in the furnace the sample was quickly heated up to the temperature at which the measurement was to be performed. Typically 10 to 20 activity profiles were measured at each temperature. The symmetry of the measured activity profiles can be used as a sensitive monitor of systematic errors such as sample inhomogenities. The source position at $t = 0$ is treated as a adjustable parameter in the determination of $\sigma^2(I(x,t))$. The determination of D is not affected by resolution effects and the spatial extent of the source at $t = 0$ because these effects cancel out according to Eq. (4).

The *in situ* method used in this experiment has several advantages compared to the traditional radioactive tracer technique in which a layer of active material is deposited on the end surface of the sample, which normally is shaped as a cylinder. The sample is then heated and the radioactive tracer atoms diffuse into the bulk of the sample. The sample is sectioned after a given time of annealing, and the activity is measured in each section individually. The diffusion coefficient is determined from the spatial activity profile which is determined from the measured activity of the individual sections. Only one value of the diffusion coefficient is determined per annealing and sectioning. It is therefore a rather laborious and expensive method.

The *in situ* method is nondestructive and diffusion coefficients at several temperatures can therefore be measured using the same sample. Several activity profiles at different temperatures can be measured per irradiation of the sample. The number of profiles is limited by the half-life of the tracer nuclei and the magnitude of the diffusion coefficient. The tracer atoms are generated inside the sample and no interface problems are therefore present in this method in contrast to the traditional tracer technique. Furthermore the *in situ* method allows tracer diffusion measurements in cases where no tracer ion with sufficient long half life exists.

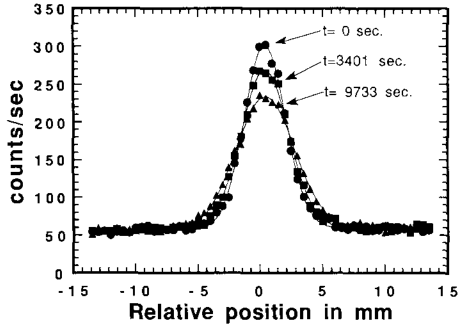

FIG. 2. Plot of selected activity profiles measured at 654 K. The profiles shown here were corrected for the decay of the ^{64}Cu nuclei. The solid curves represent a Gaussian plus a linear background fitted to the measured points.

TABLE I

DIFFUSION COEFFICIENTS AT VARIOUS TEMPERATURES FOR Cu^+ DIFFUSION IN CuCl

T (K)	*D* (cm^2/sec)
	γ-phase
583	$7.1(7) \times 10^{-8}$
608	$3.4(2) \times 10^{-7}$
624	$6.7(4) \times 10^{-7}$
654	$1.56(3) \times 10^{-6}$
674	$3.1(4) \times 10^{-6}$
	β-phase
688	$2.46(8) \times 10^{5}$
693	$2.8(1) \times 10^{-5}$

3. Results

Activity profiles were measured at 583, 608, 624, 654, and 674 K in the γ-phase and at 415 and 420 K in the β-phase. Data analysis was performed by least-squares fitting of a Gaussian plus a linear or, in some cases, a parabolic background function to the measured profiles. No asymmetry in any of the measured profiles was observed, which shows that the time needed for scanning a profile is negligible compared to the rate of diffusion. Selected activity profiles measured at 387°C are shown in Fig. 2. Plots of $\sigma^2(I(x,t))$ vs t are shown in Fig. 3, and the diffusion coefficients are determined from the slope of these curves by aid of Eq. (4). The measured diffusion coefficients are given in Table I and plotted as log D vs 1000/T in Fig. 4. Points belonging to the γ-phase are falling on a straight line, indicating that the diffusion in this phase can be described by an Arrhenius equation

$$D = D_0 e^{-E_a/k_B T}, \qquad (5)$$

where E_a is activation energy and k_B is Boltzmann's constant. The activation energy for diffusion in the γ-phase was found to be

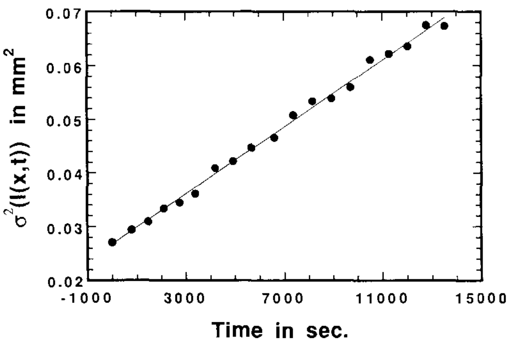

FIG. 3. Plot of $\sigma^2(I(x,t))$ versus time for activity profiles measured at 654 K.

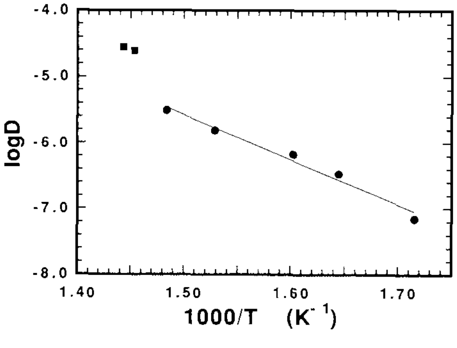

FIG. 4. Plot of log D versus 1000/T. Points marked with ● and ■ belong to the γ- and β-phase, respectively. The points in the γ-phase were fitted to an Arrhenius equation (solid line).

1.4(1) eV with the preexponential factor $D_0 = 4.557(2) \times 10^4$ cm²/sec. The β-phase is stable over a rather narrow temperature range, and only 2 points were measured in this phase. A reliable determination of the activation energy in this phase is therefore not possible.

The diffusion coefficients measured in γ-phase of CuCl are somewhat higher than the corresponding values for γ-phase CuI, which vary from 1.0×10^{-7} to 4.1×10^{-7} cm²/sec for temperatures in the range 588 to 623 K, and the activation energy for diffusion in γ-phase CuI is 1.30 eV (7). Taking into account that iodine ions are considerably larger than chloride ions, it is therefore rather surprising that the activation energy of 1.4(1) eV found for γ-phase CuCl in this study is so close to the corresponding value for CuI. Electrochemical measurements yields a value of 1.11 eV for the activation energy for diffusion in γ-phase CuCl at temperatures above 403 K, which is in reasonable agreement with the value obtained in this study. From Table I it is seen that a sharp increase in the diffusion coefficient is associated with the transition from the γ- to the β-phase. Similar discontinuities in the diffusion coefficient are also observed at the structural phase transitions in CuI, and it is generally a well known phenomena in many fast ionic conducting compounds. The diffusion coefficients measured in β-phase CuCl are of the same magnitude as the Cu^+ diffusion coefficients in molten CuCl and in α-phase CuI (*7, 10*). A comparison of the diffusion coefficients in α-phase CuI and β-phase CuCl is justified by the fact that the β-phase of CuCl falls within the temperature range where the α-phase of CuI is stable. Both phases have a close packed arrangement of the anions, but the crystal systems are hexagonal (β-CuCl) and cubic (α-CuI), respectively, as mentioned in the Introduction. Powder neutron diffraction studies have shown that the Cu^+ ions are randomly distributed over all the tetrahedral sites and part of the Cu^+ ions are also located in octahedral holes (*2*). Both phases of CuCl have also been studied by powder neutron diffraction. The cation distribution in the β-phase could unfortunately not be derived from these data (*11*). Taking into account the similarities between hexagonal and cubic close packing, it is likely that the cation distribution as well as diffusion pathways are very similar in the two phases.

An *in situ* tracer diffusion study of the diffusion in three phases of CuBr will be performed in the near future. Combining the diffusion coefficient measurements with molecular dynamics simulations of the complete series of copper halides should improve the understanding of the differences in interatomic potentials and ionic transport properties in this series of compounds.

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