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SUPERIONIC CONDUCTORS

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1. Introduction

The terms "Superionic conductors" (SIC), "Fast Ion Conductors" or "Solid Electrolytes" have been introduced to denote solid materials exhibiting anomalously high ionic conductivity. This conductivity approaches in some cases the value of 1 ohm^{-1} cm^{-1} at room temperature being thus comparable to that of good liquid electrolytes. In recent years the interest in such materials has grown perceptibly due to the wide range of potential application, mostly in the production and storage of energy.

There are several good definitions of SIC but the most general seems to be Zeyher's[1]: a SIC is an ionic compound whose ions may be divided into two groups according to their dynamic behavior. The ions of the first group (usually cations) cannot be localized near a definite lattice site and make both oscillatory and diffusive motions. The ions of the second group perform small oscillations around the sites of a regular periodic lattice. A SIC thus contains a fluid-like part which is exposed to a periodic potential of a solid-like part. Both subsystems interact and mutually perturb each other's motions.

This article aims to give a brief review of the properties of the materials embraced by this definition. Included is a survey of results attained at the author's Institute.

2. Correlation Between the Structure and Superionic Conductivity

Ionic conductivity as high as one reciprocal ohm centimeter cannot be normally induced by the mechanism found in conventional ionic conductors, i.e. by the thermal generation of lattice

defects and the transport of ions over them. This mechanism can mobilize only 10^{-4} to 10^{-1} per cent of the entire number of ions as charge carriers. In a typical SIC this yield is much larger: 1 - 10%, giving thus a conductivity up to 10^5 times higher than in a conventional ionic conductor. Also, the explanation for a very small activation energy needed was not to be found within the framework of older theories of ionic conductivity. In some cases it may be as small as hundredths of eV giving an unusually flat temperature dependence of the conductivity. These facts suggest that diffusion process in a SIC is related to its structure rather than to the thermal defects.

Indeed, the first informations on the nature of SIC stem from the structure analysis. Rahlfs[2] investigated a series of I-VI compounds (silver and copper sulfides, selenides and tellurides), while Strock[3] and Buerger and Wuensch[4] studied silver iodide, AgI. They arrived at more or less the same picture best represented by an electron density map (e.g. of cuprous sulfide, Cu_2S[4]). The contours of this map, as we know, indicate the average electron density and thus the ionic occupation at various places in a lattice. As for Cu_2S, the map clearly showed that sulfur ions have well defined locations. At the same time the copper ions are distributed rather uniformly along paths which extend between what would normally considered the crystallographic sites. Evidently, this picture leads directly to the definition of SIC given in Introduction stating a well formed anion sublattice filled with a "molten" cation system.

Let us note some further details of the structure of a SIC examplified by AgI, frequently regarded as a prototype. Strock[3] found in it a bcc configuration of iodine ions. Two Ag-ions per unit cell are statistically (randomly) distributed ove 42 positions. There are thus many more equivalent sites than silver ions. If the sites are really equivalent in energy such a structure is usually called "average"[5].

According to Armstrong and coworkers[6] a random distribution of ions over a large number of sites or "averageness" of a structure is of drastic consequence to the concentration of charge carriers n in the unipolar ionic conductivity $\sigma = Zen\mu$ (Z is the valence of the carriers, μ their mobility and e electronic

charge). They found that the concentration n is given by

$$n \sim \left[(n_i + n_L)N_i/(N_i + N_L)\right] \exp(-E_t/kT) \qquad (1)$$

Here E_t is the activation energy, N_L and N_i are the concentrations of normal lattice sites and equivalent interstitial sites, respectively, while n_L and n_i are the concentrations of ions in the respective sites. An average structure or a random distribution is reflected in (1) if $E_t = 0$. We see then that distinction between normal and interstitial sites ceases to exist. There is a total concentration of sites $(N_L + N_i)$, of which $N_L = n_L + n_i$ is the concentration occupied. Charge carrier concentration n is essentially given by the ratio $N_i/(N_L + N_i) = N_i/(n_L + n_i + N_i)$. If the number of equivalent sites is much larger than that of ions this ratio approaches one, which means that <u>all</u> cations are able to be charge carriers. The difference between conventional and superionic conductors appears here to be significant indeed.

Ionic conductivity, however, is not given only by n but by mobility μ as well. For this quantity Armstrong et al. used the expression

$$\mu \sim \exp(-E_m/kT) \qquad (2)$$

in which E_m is the activation energy for movement of ions. As in the classical problem of ionic conduction a high value of μ and σ may be expected only in the crystals where E_m has low values.

The extent of this article does not allow a detailed analysis of Armstrong, van Gool and others. Instead, let it be stated briefly that the low values of E_t and E_m may be found in those ionic compounds with monovalent cations. They must be stable in various coordinations i.e. they must have almost the same energy if coordinated by 4, 3 and 2 other ions.

These conditions are not at all general. They cannot embrace all classes of SIC but, at least, explain the outstanding place taken by some silver and copper salts. They also led to the formulation of more general criteria a compound should satisfy to be regarded as a SIC. These four criteria are as follows:

1. The activation energy E_t should be small. This means that the energies of cation-anion interactions in the different sites should be similar.

2. A large excess of site should be available for cations. If so, almost every ion is surrounded by empty places and a great deal of cations are mobile.

3. The potential barrier E_m to the motion of the ions should be low.

4. The structure should consist of continuous chains of facesharing polyhedra through which the ions can diffuse in one, two or three dimensions.

The last condition is fairly obvious. It assures an unhindered transport of ions through a macroscopic crystal.

3. Some of the Current Problems

The conclusions of the foregoing paragraph give only a very rough description of the nature of SIC. It is in fact more complicated and there is, as yet, no simple theory explaining all SIC properties. Many results formerly accepted as plausible are now abandoned after critical analyses prompted by new data. besides the fact that the four criteria formulated above have been developed having in mind primarily silver and copper salts, the results inside a certain group of SIC are also inconsistent. For example, such a basic datum as the structure of AgI seems to be still under question. Strock's 42 positions thus appear to be only one choice among several possible[7]. H.Burley showed in addition that even in strock's structure the occupation of all sites cannot be equal. A truly random distribution of silver ions therefore, does not exist. Seemingly it is obvious, as a statistical distribution of cations assumes no interaction between them, which certainly is not true in an ionic compound. But on the other hand, some direct measurements[9] confirmed the existence of almost completely average structures. The high-temperature phases of $Ag_{2+x}S$ and $Ag_{2+x}Se$ are good examples.

The concept of molten cation sublattices is not quite clear either. After Strock and Rahlfs this attractive idea has been

used frequently for several reasons. Unfortunately, theoretical interpretation of liquids is not simple. Many more difficulties are to be expected in interpretation of a "liquid" placed inside of a more or less rigid but interacting anion sublattice. To apply a certain model one needs a statement about the characteristic time intervals i.e. about the length of the transition time of an ion as compared to its mean residence time. There are suggestions that in AgI these times are of the same order.[10]

This has been illustrated by several effective experiments. All of them have shown both the oscillations and translational motion of cations. For example, the dynamic or frequency dependent conductivity of the high-temperature phase of AgI shows a pronounced resonance near $\nu \approx 100\ cm^{-1}$. This resonance is due to oscillations of Ag-ions about preferred lattice sites or inside some potential barriers. On the other hand, the spectral response at lower frequencies is enhanced compared to that of a conventional ionic conductor, reflecting the high value of static conductivity[11]. A few theoretical models are now under development. All of them try to find a unified basis for both the oscillating and diffusing motions of the cations[10,12,13].

4. Phase Transitions in Superionic Conductors

Several times so far we have stressed some conclusion or a result as related to the high-temperature phase of a SIC, tacitly assuming the phase transitions. Indeed, a great majority of SIC undergo one or two transitions. A comprehensive classification of them was done by Pardee and Mahan[12]. Surveying the available data they concluded that SIC commonly have two kinds of phase transitions: Class I and Class II. Class I transitions are those with a discontinuity in the ionic conductivity. They are first order and have a latent heat. Often they are accompanied by changes in the lattice symmetry. Since the rapid conductivity changes are of 2 or 3 orders of magnitude, the authors invented the term "insulator-electrolyte" transitions.

Class II transitions are second order with lambda specific heat and continuous ionic conductivity which changes only its activation energy. With an elaborate theoretical model Pardee

and Mahan argued that every SIC (except for ceramic oxides) must have a Class II (order-disorder) phase transition. Silver iodide may again be used as an illustrative example. Its transition at $T_1 = 143^{\circ}C$ (regularly, and in their opinion eroneously referred as a transition to a SIC state) is qualified as a transition to the state with a small order parameter. This will not fall to zero before the second transition temperature T_2. Silver iodide does have another phase transition at $T_2 = 430^{\circ}C$. It should be ascribed to nothing but the disordering of the silver subsystem. Rubidium silver iodide, $RbAg_4I_5$ is another such case, with $T_1 = -150^{\circ}C$ and $T_2 = -64^{\circ}C$. There are, however, some important exceptions to the Bardee-Mahan's theory. Notably there is Ag_2HgI_4 with a $54^{\circ}C$ phase transition which is second order but also with a discontinuity in the ionic conductivity, and sodium beta alumina with no phase transitions whatsoever.

Recent theory of Lam and Bunde[13] seems to be more general. It recognizes a possibility of SIC having either a) no phase transitions, or b) one phase transition (first or second order), or c) two transitions. In the cases b) and c) the structure change of the anion lattice may occur. Evidently, if more details of the very complicated interactions in a SIC are taken into account, the results which appear correspond much closer with the actually observed properties.

This may be the place to mention a result of DTA on $Cu_{2-x}Se$ samples which introduces new data into the discussion. It appears that a first order phase transition may gradually become second order varying only the stoichiomatry of the compound[14].

5. A Short Survey of Superionic Conductors

So far over 300 different compounds or classes of compounds are listed as having high ionic conductivity.[15] All of them, however, cannot be treated as SIC in the sense of this article. Many are simply good but still conventional ionic conductors, while some others are transitional forms between the two. To date true SIC properties are still to be found only in silver, copper and some alkali salts, and the term SIC could be reserved for them only. For the entire field of compounds with unusually high

ionic conductivity the term "solid electrolytes" seems more appropriate.

Perhaps a further clarification is in order here. Although the terms "SIC" or "solid electrolytes" have been introduced to stress the high values of ionic conductivity, we feel that the compounds with mixed conduction should not be excluded. As such materials are of similar value in application, there is no reason to classify them apart.

Of 300 compounds only about 80 have been experimentally investigated. Half of these were found to exhibit semiconducting or metalic electronic conduction, leaving approximately 40 compounds with a purely ionic conductivity. 26 of them have sigma higher than 10^{-3} $ohm^{-1}cm^{-1}$ at room temperature which is usually regarded as a lower limit for succesful application. Silver and copper ion conducting materials are dominating (19) while the remaining 7 are alkali ion conductors.

Almost all members of silver group compounds are based on silver iodide. They are synthesized with a goal of stabilization of the high-temperature, SIC phase at room temperature to facilitate their employment. Two approaches have been used: a) the substitution of anions (with S^{2-}, PO_4^{3-}, SO_4^{2-}, WO_4^{2-} etc.) and b) the substitution of cations (with Na, K, Rb etc.). The latter approach gave the famous compound $RbAg_4I_5$ with the highest ionic conductivity at room temperature so far (0.12 $ohm^{-1}cm^{-1}$). Among silver salts very high conductivities are also found in high-temperature phases of Ag_2S and Ag_2Se (as high as 4 $ohm^{-1}cm^{-1}$ at 200^oC) but they are masked by pronounced electronic conduction due to doping activity of stoichiometric deviations.

Much effort has been concentrated on the synthesis or "design' of the SIC with anionic, mostly oxygen conduction. The main reason for the effort is the prospective application in the high temperature fuel cells and in the oxygen activity sensors in various industrial processes. Zirkonia ZrO_2, hafnia HfO_2 and thoria ThO_2 doped with CaO, Sm_2O_3, Y_2O_3 etc. are examples of such conductors. Doping in them stabilizes the fluorite structore and introduces a large number of anion vacancies preserving electrical neutrality. Oxygen conduction accurs via these vacancies. Ionic conducductivities are of the order of 0.1 $ohm^{-1}cm^{-1}$ at 1000^oC. A development of carbon, nitrogen and sulfur ion conducting compounds may be expected in the future.

From the standpoint of application the alkali ion conductors are of the greatest importance. In contrast to silver salts which suffer from several disadvantages (stability, economy) alkali ion conductors deserve much more attention. The highly electropositive ions provide the possibility of large solid state cell voltages and high energy densities. Among many materials under vigorous investigation the most attractive is the family of compounds called beta alumina. It has the general formula $M_2O.11Al_2O_3$ (M = Na, K, Li, Ag) and a unique structure consisting of hexagonal blocks with a spinel-like configuration of oxygen and aluminium ions. Among the blocks the layers are interspersed containing only oxygen and e.g. sodium. Oxygen ions are rigid, while sodium ions, having twice as many places as their number are very mobile through the layers. In fact the alkali beta alumina is a SIC with two-dimensional conduction. Extreme chemical stability, good mechanical properties, and, of course, high ionic conductivity (about 0.01 $ohm^{-1}cm^{-1}$ at room temperature) make beta alumina a very promising material. For a novel and interesting example of sodium beta alumina use in a highly efficient converter of thermal (solar) energy see Weber[16].

Let us close this survey with a remark on proton conductors. They may find an important application in low-temperature fuel cells. Despite much effort only a few solid compounds exhibiting proton conduction have been found so far - none of them with the characteristics of a SIC.

6. Contributions of Institute of Physics, Zagreb

A rather diverse scientific programme of the Institute is partly devoted to SIC. A lot of experimental work has been done in the last few years, mostly concerned with chalcogenides $Cu_{2-x}Se$, $Ag_{2+x}Se$ and $Cu_{2-x}Ag_xSe$[17-28]. These comparatively unknown compounds proved to be a rich source of interesting information on two counts: their SIC characteristics, and the semiconductor properties. As mentioned before, cuprous selenide offers a new variable in experimental investigation - the possibility of change to stoichiometry in a very wide range. This feature, uncommon in SIC materials, enables one to, for example,

change a fundamental characteristic of a SIC - the ratio of available site concentration to the concentration of cations. The temperature of the phase transition to the SIC state may also be changed by stoichiometry. It can be lowered from 140°C down to below the room temperature. Such a low critical temperature makes cuprous selenide unique among silver and copper salts. From the standpoint of the electronic conductivity the phase transitions are still unexplained. Yet it is obvious that the conductivity behaves anomalously. An effort has been made to interpret this behavior with a special model[22], but it turned out to be an oversimplification. Besides, some recently found phase transitions occur at lower temperatures[14].

Semiconductor properties in general have been found as very simple. Stoichiometric deviations dope the crystals in such a simple manner that each deficit copper atom contributes a hole in the valence band. Just like famous cuprous sulfide, $Cu_{2-x}Se$ may thus also be used as an efficient hole injector in various heterostructures. Concerning the permanent stoichiometric deviations in cuprous selenide, they can be annichilated only by mixing with $Ag_{2+x}Se$, forming $Cu_{2-x}Ag_xSe$ crystals. This has been proved detecting a metal-nonmetal transition in them[27].

Two recent papers outside the field of chalcogenides and concerning the general properties of SIC are worth mentioning. First[29] deals with the Madelung constant of a SIC. This constant has been calculated for both the ordered crystals and the amorphous systems. For a partially disordered system, as a SIC is, it had not been evaluated. Our results give the Constant for various SIC and show that in some cases it may be temperature dependent. The second paper[30] shows that the liquid-like cation subsystem in a SIC may be disturbed by forces other than electrical, specifically that a concentration gradient may be formed in a high centrifugal field. Some applications of this effect are also suggested.

We hope the work on SIC in the Institute will be continued in the future. A newborn cooperation with some workers in "Jožef Stefan" Institute, Ljubljana will certainly promote it.

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