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**STUDY OF MULTICOMPONENT DIFFUSION AND
TRANSPORT PHENOMENA**

**ANNUAL PROGRESS REPORT
FOR PERIOD 7/1/91-6/30/92**

**Hiroshi Sato
School of Materials Engineering
Purdue University
West Lafayette, IN 47907**

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I. Summary of Scientific Progress

A steady progress is being made in all areas of research proposed for this period. Indeed, an exciting progress is now expected in the frequency dependence of ionic conductivity and in atomistic treatments of chemical diffusion based on the progress made in this period. In the following, a brief account of work done during this period (February, 1991 - January, 1992) is given.

1. Application of the Cluster Variation Method for the Calculation of the Percolation Problem

The problem whether β -alumina type compounds can become mixed conductors by doping mixed valent ions was treated by the Cluster Variation Method. The same problem was treated by a higher degree of approximation this time and was presented at the SSI (Solid State Ionics) - 8 meeting held in October, 1991 at Lake Louise, Alberta, Canada (paper #6). Based on the assumption that the electronic conduction in β -alumina is due to the hopping of small polarons to the nearest neighboring ions on the octahedral sites in the spinel block similar to that in magnetite, the triangle-tetrahedron approximation of the Cluster Variation Method gives the percolation threshold of 0.39 for the required concentration of mixed valent ions on the octahedral sites compared to the value 0.24 obtained by the pair approximation. A specific interest of this work is, in addition to the intrinsic interest in making β -alumina type compounds a mixed conductor, to treat a percolation problem in the specific two dimensional conduction layers consisting of two Kagome layers connected by a middle triangular lattice layer in the β -alumina type structure.

2. Atomistic Treatments of Chemical Diffusion

The basis for chemical diffusion process has been first established by Darken by means of irreversible thermodynamics. However, Darken's formalism corresponds to the molecular field approximation of the problem. This is due to the fact that the formalism of irreversible thermodynamics deals with the motion of a homogeneous assembly rather than the average of the time correlation of the motion of individual particles. In order to deal with such a problem, it is necessary to treat the problem by statistical mechanics from an atomistic point of view.

Even in the atomistic approach, we found that the original PPM gives a similar result to that of Darken even in the pair approximation. This difficulty is found to be removed by the application of the time conversion process based on the pair approximation of the PPM.

The point approximation (molecular field approximation) of the PPM is, on the other hand, self consistent and does not require the time conversion process. Although this is equivalent to the Darken's approach, we treated the chemical diffusion process in ternary systems with the point approximation from an atomistic point of view in order to examine the feasibility of the treatment by the atomistic approach in the higher approximation. The papers #1 and #2 represent these results.

3. Frequency Dependence of Ionic Conductivity

As stated in the research program for this funding period, the major aim of this project is to understand the mechanism of the relaxation process generally observed in structurally disordered solid electrolytes. The process is often termed "universal dielectric response" if the frequency dependence of conductivity and permittivity is considered. The relaxation process shows distinct non-Debye characteristics. At this moment, no appropriate analytical theory exists to explain this behavior.

We found that the pair approximation of the PPM with the time conversion process essentially deal with this problem appropriately (paper #5 which was presented at SS1-8 meeting, last October). Although numerical calculations for individual cases are yet to be made, this work represents the most exciting progress made this year.

4. Diffusion Process in Semiconductors

Although the formulation of diffusion equations characteristic to semiconductors is completed, the cluster size required for a systematic treatment by the PPM of a variety of problems in semiconductors becomes extremely large and we found this makes the analytical treatment not feasible. Because of exciting progress in the treatment of frequency dependence of ionic conductivity and in atomistic chemical diffusion, the effort on this project is reduced at this moment.

5. Formalism of the Path Probability Method

Upon the invitation from the Japan Institute of Metals, a review paper "Path Probability Method of Irreversible Statistical Mechanics" was written for Materials Transactions, JIM (paper #4). Here, the formalism of the Path Probability method is examined in order to explore the applicability of the method to a variety of kinetic problems, especially to transport problems. This work was instrumental to the progress of the research on the frequency dependence of ionic conductivity.

6. Theoretical Aspects of Mixed Alkali Effect

Upon the invitation of the American Ceramic Society, a review paper "Theoretical Aspects of Mixed Alkali Effect" was written in Ceramic Transactions, Vol. 20, Glasses for Electronic Applications (paper #3). Here, it is shown that, by means of the pair approximation of the PPM with time conversion, how general characteristics of mixed alkali effects can be

explained as general characters of ionic conductivity in interacting binary systems. Here, the concept of percolation efficiency defined by the ratio of the ionic conductivity at zero frequency and at infinite frequency $\sigma(0)/\sigma(\infty)$ plays an important role. Therefore, the study of the frequency dependence of ionic conductivity constitutes an important part of the study of mixed alkali effect.

II. List of Publications

1. H. Zhang, A. Datta and H. Sato, "Atomistic Treatment of Chemical Diffusion in Multicomponent Alloys: Relation between Intrinsic Diffusion Coefficient and Diffusion Coefficients in the Laboratory Frame," in Atomic Migration and Defects in Materials, edited by D. Gupta, H. Jain and R. W. Siegel, Sci-Tech Publication (1991) pp. 107-114.
2. H. Sato and A. Datta, "Atomistic Treatment of Chemical Diffusion Phenomena," in Atomic Migration and Defects in Materials, edited by D. Gupta, H. Jain and R. W. Siegel, Sci-Tech Publication (1991), pp. 115-120.
3. H. Sato, "Theoretical Aspects of Mixed Alkali Effect," Ceramic Transactions, Vol. 20. Glasses for Electronic Applications, ed. K. M. Nair, The American Ceramic Society (1991), pp. 19-39.
4. H. Sato, "Path Probability Method of Irreversible Statistical Mechanics: An Overview." Materials Transactions, JIM (1991), 32 (1991), pp. 509-525.
5. H. Sato, T. Ishikawa and K. Funke, "Frequency Dependence of Ionic Conductivity in Interacting Lattice Gas Systems," Solid State Ionics (accepted).
6. A. Datta, R. Kikuchi and H. Sato, Percolation Threshold for Electronic Conduction in β -Alumina Type Compounds, II, Solid State Ionics (accepted).

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