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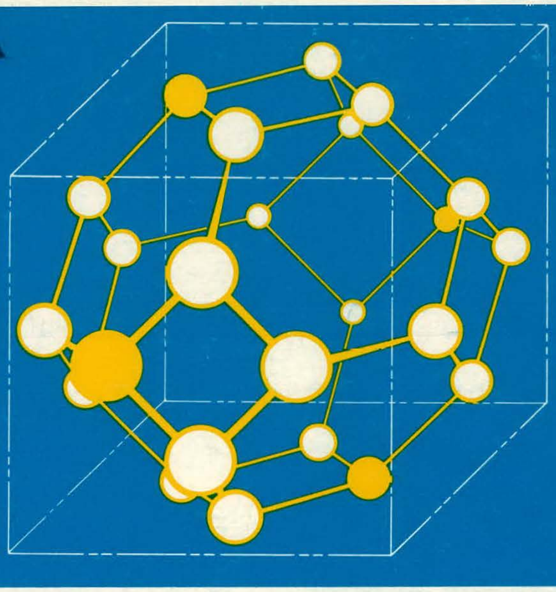

PROGRAM AND ABSTRACTS

International Conference

Fast Ion Transport In Solids

Lake Geneva, Wisconsin, U.S.A.
May 21-25, 1979

ORGANIZING COMMITTEE

Co-Chairmen: J. N. Mundy and P. Vashishta
Argonne National Laboratory

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PROGRAM AND ABSTRACTS
~~for the~~
International Conference
on
FAST ION TRANSPORT IN SOLIDS:
ELECTROLYTES AND ELECTRODES.

M

May 21 - 25, 1979

ABBEY HOTEL AND CONFERENCE CENTER
LAKE GENEVA, WISCONSIN

Conference Planning and Management:	Mrs. Miriam Holden Office of Public Affairs Argonne National Laboratory
Conference Secretaries:	Mrs. Mary Ann Dillon Miss. Karen Abbott Argonne National Laboratory

MONDAY, May 21, 1979

8:30 A.M. Welcome and Introduction to Conference

SESSION 1 8:45 A.M. Chairman: D. C. L. Price, Argonne National Laboratory

I-1	Overview of Basic and Applied Research on Battery Systems at Argonne	M. V. Nevitt Argonne National Laboratory
I-2	Role of Basic Research in our Energy Future	J. S. Kane U. S. Department of Energy
I-3	Layer and Tunnel Compounds--Fast Ion Transport and Electrochemical Energy Storage	M. S. Whittingham EXXON

10:30 A.M. COFFEE

SESSION 2 11:00 A.M. Chairman: D. K. Stevens, U. S. Department of Energy

I-4	Lithium/Metal Sulfide Battery Development	R. Steunenberg Argonne National Laboratory
I-5	Sodium/Sulphur Traction Batteries - A Review of Progress and Problems in their Development	R. J. Bones AERE Harwell, United Kingdom

12:30 P.M. LUNCH

SESSION 3 2:00 P.M. Chairman: P. A. Nelson, Argonne National Laboratory

I-6	Advanced Battery Program in General Electric	J. A. Asher General Electric
I-7	Precision Analysis of the Li-TiS_2 Battery	A. H. Thompson EXXON
I-8	Evaluation of Properties Related to the Application of Fast Ionic Transport in Solid Electrolytes and Mixed Conductors	R. A. Huggins Stanford University

3:30 P.M. COFFEE

SESSION 4 4:00 P.M. Chairman: N. Weber, Ford Laboratories

I-9	Ambient Temperature Solid State Batteries	B. B. Owens Medtronic, Inc.
I-10	New Types of Solid Electrolyte Gas Sensors	M. Kleitz University of California and Grenoble, France
I-11	Electrochromism of Anodic Iridium Oxide Films (AIROFs)	G. Beni Bell Laboratories

6:00 P.M. DINNER

8:00 P.M. - 10:00 P.M. POSTER SESSION PA

TUESDAY, May 22, 1979

SESSION 5 9:00 A.M. Chairman: B. J. Wuensch, Massachusetts Institute of Technology

I-12	Ordering of the Conducting Ions in Silver β-Alumina	R. Comes University of Paris-Orsay, France
I-13	Neutron Diffraction Studies of Beta Aluminas and other Ionic Conductors	B. C. Tofield AERE Harwell, United Kingdom
I-14	Structure Investigations of Superionic Conductors: Requirements, Results and New Questions	F. Reidinger Brookhaven National Laboratory

10:30 A.M. COFFEE

SESSION 6 11:00 A.M. Chairman: J. P. Remeika, Bell Laboratories

I-15	Effect of Pressure and Composition on Fast Na^+-Ion Transport in the System $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$	J. A. Kafalas Lincoln Laboratory
I-16	Neutron Diffraction of Doped Bi_2O_3 and Li_4SiO_4 and Related Studies	B. E. F. Fender Oxford University, United Kingdom
I-17	Factors Affecting Ion Mobility in Substitution Intercalation Compounds in Chalcogenide Hosts	J. Rouxel University of Nantes, France

12:30 P.M. LUNCH

SESSION 7 2:00 P.M. Chairman: W. Van Gool, State University-Utrecht, Netherlands

I-18	Poly-Ethers as Solid Electrolytes	M. B. Armand St. Martin d'Heres, France
I-19	Topochemical Reactions of Metal Oxides with Lithium	D. W. Murphy Bell Laboratories
I-20	High Alkali Ion Conductivity in Rapidly Quenched Oxides Containing No Network Formers	A. M. Glass Bell Laboratories

3:30 P.M. - 5:30 P.M. POSTER SESSION PB

6:00 P.M. COCKTAILS

7:00 P.M. BANQUET

WEDNESDAY, May 23, 1979

SESSION 8 9:00 A.M. Chairman: J. Kennedy, University of California

I-21	Diffusion and Ionic Conductivity in Solid Electrolytes	J. N. Mundy Argonne National Laboratory
I-22	Fast Ion Conducting Gallates and Aluminates-Similarities and Differences	L. M. Foster IBM
I-23	Studies of Ionic Motion in Mixed Na-Li β-Alumina	R. E. Walstedt Bell Laboratories

10:30 A.M. COFFEE

SESSION 9 11:00 A.M. Chairman: H. Sato, Purdue University

I-24	Ionic Transport in Some Fluorite-Structured Solid Solutions	J. Schoonman State University-Utrecht, Netherlands
I-25	New Solid Electrolytes with High Ionic Conductivity	P. Hagenmuller Lab. Chimie du Solide du CNRS, France
I-26	Neutron Spectroscopy and Fast Hydrogen Diffusion in BCC Transition Metals	D. Richter Brookhaven Nat'l Lab. and KFA Julich Germany

12:30 P.M. LUNCH

SESSION 10 2:00 P.M. Chairman: H. U. Beyeler, Brown Boveri, Switzerland

I-27	The Low-Energy Excitation Spectra of Li, Na, K and Ag β-Alumina	A. C. Anderson University of Illinois
I-28	Theory of Microwave Conductivity in Superionic Conductors	L. Pietronero Brown Boveri, Switzerland
I-29	Molecular Dynamics Studies of Superionic Conductors	A. Rahman Argonne National Laboratory

3:30 P.M. COFFEE

SESSION 11 4:00 P.M. Chairman: K. Funke, University of Gottingen, West Germany

I-30	NMR Studies of Solid Electrolytes and Solid Solution Electrodes	C. Berthier University of Grenoble, France
I-31	Hydrodynamics of Superionic Conductors	R. Zeyher MPI Stuttgart, Germany

6:00 P.M DINNER

8:00 P.M. - 10:00 P.M. POSTER SESSION PC

THURSDAY, May 24, 1979

SESSION 12 9:00 A.M. Chairman: A. Lunden, Chalmers Technical University, Sweden

I-32	In^+ and Tl^+ Transport in Halide Lattices	D. F. Shriver Northwestern University
I-33	Recent Development in Solid Silver and Copper Ion Conductor Materials	T. Takahashi Nagoya University, Japan
I-34	Nature of Ionic Motions in AgI and CuI	P. Vashishta Argonne National Laboratory

10:30 A.M. COFFEE

SESSION 13 11:00 A.M. Chairman: B. Baranowski, Polish Academy - Warsaw, Poland

I-35	Raman, Infrared, Neutron Diffraction and Ionic Conductivity Studies of Beta"-Aluminas	J. B. Bates Oak Ridge National Laboratory
I-36	EXAFS Investigation of Superionic Conduction	J. B. Boyce XEROX
I-37	The Role of Correlated Motion in Superionic Conductors	T. Geisel XEROX and University of Regensburg, Germany

12:30 P.M. LUNCH

SESSION 14 2:00 P.M. Chairman: D. H. Whitmore, Northwestern University

I-38	Low Frequency Light Scattering from the Cuprous Halides	R. J. Nemanich XEROX
I-39	High Pressure Studies of Fast Ion Conductors of the Mercury and Silver Iodide Type	J. R. Ferraro Argonne National Laboratory
I-40	Dynamical and Critical Point Properties of $RbAg_4I_5$	M. B. Salamon University of Illinois
I-41	Diffusion and Conductivity in Superionic Conductors	C. P. Flynn University of Illinois

5:00 P.M. BOAT TRIP

7:00 P.M. BAR-B-Q

FRIDAY, May 25, 1979

SESSION 15 8:30 A.M. Chairman: W. L. Worrell, University of Pennsylvania

I-42	Effect of Additives and Moisture on the Ionic Conductivity of Li_5MO_4 (M=Al,Ga,Fe)	R. T. Johnson, Jr. Sandia Laboratories
I-43	Vitreous Solid Electrolytes	B. Scrosati University of Rome, Italy
I-44	Electrochemical Properties of Some Solid Lithium Electrolytes	U. v. Alpen MPI-Stuttgart, Germany

10:00 A.M. COFFEE

SESSION 16 10:30 A.M. Chairman: J. B. Wagner, Jr., Arizona State University

I-45	Structure and Ion Transport in β'' Alumina	W. L. Roth General Electric and Grenoble, France
I-46	Chemistry and Conductivity of Protonic Beta Aluminas	G. C. Farrington General Electric
I-47	Thermodynamic and Transport Properties of Selected Solid Solution Electrodes	B. C. H. Steele University of London, United Kingdom

12:00 A. M. LUNCH

2:00 P.M. BUSES TO AIRPORT

POSTER SESSION-PA 8:00 P.M. Monday, May 21, 1979

PA-1 R. T. Dirstine and W. O. Gentry, FABRICATION OF β''-Al_2O_3 TUBES FROM CAST CERAMIC TAPE

PA-2 G. R. Miller, B. J. McEntire, T. D. Hadnagy, R. S. Gordon and A. V. Virkar, PROCESSING AND PROPERTIES OF SODIUM β''-ALUMINA AND NASICON CERAMIC ELECTROLYTES

PA-3 A. V . Virkar and G. R. Miller, DEGRADATION OF RAPID ION CONDUCTORS UNDER ELECTROLYTIC CONDITIONS

PA-4 S. R. Tan and G. J. May, THE HEAT TREATMENT OF BETA-ALUMINA

PA-5 H. Kuwamoto, Y. Hirotsu and H. Sato, SHORT PERIOD β-ALUMINA TYPE COMPOUNDS

PA-6 T. K. Hunt, N. Weber and T. Cole, SODIUM β''-ALUMINA AT HIGH CURRENT DENSITY

PA-7 N. Weber, Terry Cole and T. K. Hunt, ELECTRICAL RESISTIVITY OF BETA-ALUMINA SOLID ELECTROLYTES FROM 200 to 1000 C

PA-8 W. C. Dautremont-Smith, G. Beni and J. L. Shay, ALL SOLID STATE ELECTROCHROMIC CELL BASED ON ANODIC IRIDIUM OXIDE FILMS (AIROFs)

PA-9 C. E. Rice, IONIC CONDUCTION IN ELECTROCHROMIC ANODIC IRIDIUM OXIDE FILMS

PA-10 R. Aronsson, B. Heed, B. Jansson, A. Lunden, L. Nilsson, K. Schroeder, and C. A. Sjöblom, RECENT STUDIES OF SULFATE-BASED SOLID ELECTROLYTES

PA-11 B. B. Owens, D. F. Untereker and P. M. Skarstad, LOW TEMPERATURE DEGRADATION IN THE SOLID STATE BATTERY $Ag/RbAg_4I_5/I_2$

PA-12 T. M. Gür and R. A. Huggins, DECOMPOSITION OF NITRIC OXIDE USING SOLID STATE ELECTROLYTE

PA-13 T. M. Gür, I. D. Raistrick and R. A. Huggins, SOLID ELECTROLYTE/ POROUS ELECTRODE KINETICS

PA-14 W. Weppner and R. A. Huggins - THERMODYNAMIC PROPERTIES OF THE SOLID ELECTROLYTE $LiAlCl_4$

PA-15 D. A. Stevenson, B. Heshmatpour and F. K. Moghadam, USE OF SOLID OXIDE ELECTROLYTES FOR THE STUDY OF OXYGEN SOLUBILITY AND DIFFUSIVITY IN LIQUID METALS

PA-16 L. D. Yushina, S. V. Karpachev, and W. I. Terekhov, NEW TYPE OF CAPACITORS

PA-17 S. S. Gishin - ABOUT SOME STUDIES IN ACCELERATED ELECTROFORMING OF PLUMB ACCUMULATOR PLATES

PA-18 S. Basu, and W. L. Worrell, CHEMICAL DIFFUSIVITY OF LITHIUM IN Li_xTaS_2 and Li_xTiS_2 AT $30^{o}C$

POSTER SESSION-PA: 8:00 P.M. Monday, May 21, 1979

PA-19 T. Palanisamy, R. L. Kerr and J. T. Maloy, SYNTHESIS, CHARACTERIZATION AND UTILIZATION OF $M_5ErSi_4O_{12}$ COMPOUNDS AS SOLID ELECTROLYTES IN ALKALI METAL-TiS_2 CELLS

PA-20 W. van Gool and G. H. J. Broers, RECENT INVESTIGATIONS OF SOME ION-CONDUCTING OXIDES

PA-21 M. Bayard, ANALYSIS OF THE ALTERNATING CURRENT PROPERTIES OF LISICON CERAMICS

PA-22 J. Grins and M. Nygren, T. Wallin, COMPOSITIONAL DEPENDENCE OF THE IONIC CONDUCTIVITY IN THE PYROCHLORE TYPE SYSTEMS $Me_{1+x}Ta_{1+x}W_{1-x}O_6$, Me=Na, K, Tl.

PA-23 H. Y-P. Hong, CRYSTAL STRUCTURE AND IONIC CONDUCTIVITY OF A NEW NEW SUPERIONIC CONDUCTOR, $Na_3Sc_2P_3O_{12}$

PA-24 J. M. Newsam, A. K. Cheetham and B. C. Tofield, STRUCTURAL RELATIONSHIPS IN SOME SULPHATES AND ORTHOPHOSPHATES

PA-25 D. Tranqui, J. J. Capponi, J. C. Joubert, R. D. Shannon and C. K. Johnson, STRUCTURE ANALYSIS OF $Na_4Zr_2Si_3O_{12}$ AT 300°C AND 600°C IN RELATION WITH THE IONIC CONDUCTIVITY

PA-26 B. A. Boukamp, I. D. Raistrick and R. A. Huggins, USE OF LOW FREQUENCY AC MEASUREMENTS IN SOLID STATE ELECTROCHEMISTRY

PA-27 R. J. Friauf, FOUR PROBE AC CONDUCTIVITY MEASUREMENTS FOR FAST ION CONDUCTORS

PA-28 M. Kleitz and J. H. Kennedy, RESOLUTION OF MULTICOMPONENT IMPEDANCE DIAGRAMS

PA-29 D. K. Cohen, S. O. Sari and K. D. Scherkoske, THE METAL SILVER-LIQUID INTERFACE: OXIDE PROPERTIES FROM REFLECTANCE AND SCATTERED LIGHT SPECTROSCOPY

PA-30 H. H. Fujimoto and H. L. Tuller, MIXED IONIC AND ELECTRONIC TRANSPORT IN THORIA ELECTROLYTES

PA-31 E. C. Subbarao and T. V. Ramakrishnan, IONIC CONDUCTIVITY OF HIGHLY DEFECTIVE OXIDES

PA-32 J. H. W. De Wit, T. Honders and G.H.J. Broers, THE RELATION BETWEEN THE THERMOELECTRIC POWER AND THE FAST IONIC CONDUCTION IN δ-Bi_2O_3.

PA-33 W. C. Bailey, A. R. Ochadlick, Jr., H. S. Story, and G. C. Farrington, NMR STUDY OF SODIUM ION MOTION IN β''-ALUMINA

POSTER SESSION-PA: 8:00 P.M. Monday, May 21, 1979

PA-34 D. Brinkmann, M. Mali, J. Roos, H. S. Story and R. R. Dubin, STUDY OF ANOMALOUS Na IN Na_2O ENRICHED BETA-ALUMINA

PA-35 M. Villa and J. L. Bjorkstam, Na^{23} NMR AND TWO DIMENSIONAL DIFFUSION IN β-ALUMINA

PA-36 C. E. Hayes and D. C. Ailion, NMR OBSERVATIONS OF Na IONIC DIFFUSION IN Na β''-ALUMINA AND NASICON

PA-37 A. Highe, M. Polak and R. W. Vaughan, LOW TEMPERATURE STUDY OF ^{23}Na SATELLITE SPECTRA IN β-ALUMINA

PA-38 G. E. Murch and R. J. Thorn, PHYSICAL CORRELATION EFFECTS IN THE LATTICE GAS

PA-39 H. Sato and R. Kikuchi, TEMPERATURE DEPENDENCE OF HAVEN RATIO IN FAST ION CONDUCTORS AND CORRELATION EFFECTS

PA-40 J. C. Wang, J. B. Bates, T. Kaneda, H. Engstrom, D. F. Pickett, Jr., and S. Choi, MODEL STUDIES OF MIXED-ION BETA-ALUMINAS

PA-41 D. Wolf, CORRELATION EFFECTS IN NON-STOICHIOMETRIC CRYSTALS: APPLICATION TO β''-ALUMINA

POSTER SESSION-PB: 3:30 P.M. Tuesday, May 22, 1979

PB-1 C. A. Angell and L. Boehm, IONIC CONDUCTIVITY IN LITHIUM OXIDE-FLUORIDE GLASSES

PB-2 A. Avogadro, S. Manzini and M. Villa, ^{11}B LINESHAPE AND RELAXATION IN $(AgI)_x(Ag_2O\ B_2O_3)_{1-x}$

PB-3 K. Nassau and M. Grasso, ROLLER QUENCHING FOR PREPARING HIGH CONDUCTIVITY GLASSES

PB-4 D. S. Newman, D. Hazlett and K. Mucker, CROWN ETHER SOLID ELECTROLYTES

PB-5 R. R. Dubin, J. B. Bates and T. Kaneda, CHARACTERIZATION OF HEAT TREATMENT INDUCED CHANGES IN Li-Na BETA ALUMINA SINGLE CRYSTALS

PB-6 R. R. Dubin, LITHIUM MOTION AND ACTIVATION IN Li-Na BETA ALUMINA SOLID ELECTROLYTES

PB-7 S. I. Choi and F. Sonnichsen, DISTRIBITION OF IONS IN MIXED β-ALUMINA

PB-8 T. Kaneda, J. B. Bates, J. C. Wang and H. Engstrom, IONIC CONDUCTIVITY AND RAMAN SPECTRA OF Na-Li, K-Li, and K-Sn BETA-ALUMINA

PB-9 U. von Alpen, M. F. Bell, R. Bräutigam and H. Laig-Hörstebrock, SODIUM ION CONDUCTORS - NASICON AND Na-β-ALUMINA

PB-10 C. K. Chiang, A. L. Dragoo and A. D. Franklin, SLOW TRANSIENT PHENOMENON IN Y-DOPED CeO_2

PB-11 C. B. Choudhary and E. C. Subbarao, ELECTRICAL CONDUCTION IN THE CUBIC FLUORITE PHASE IN THE SYSTEM $ZrO_2 - YO_{1.5} - TaO_{2.5}$

PB-12 D. K. Hohnke, IONIC CONDUCTION IN DOPED ZIRCONIA

PB-13 A. S. Nowick, Da Yu Wang, D. S. Park and J. Griffith, OXYGEN-ION CONDUCTIVITY AND DEFECT STRUCTURE OF CeO_2 DOPED WITH CaO AND Y_2O_3

PB-14 T. van Dijk, K. J. de Vries and A. J. Burggraaf, ELECTRICAL CONDUCTIVITY IN CERAMIC SOLID SOLUTIONS OF ZrO_2-$LnO_{1.5}$ WITH Ln=Gd, Nd.

BP-15 C. Levy, D. Schleich and O. Gorochov, EXPERIMENTAL STUDY OF IONIC CONDUCTIVITY IN Cu_3VS_4 (SULVANITE)

PB-16 J. A. Little and D. J. Fray, THE PHYSICAL AND CHEMICAL PROPERTIES OF COPPER β-ALUMINA

PB-17 M. Rosso, H. Arribart, B. Sapoval and N. LeNagard, GIANT DECREASE OF Cu_3VS_4 ELECTRONIC CONDUCTIVITY IN IONIC SOLUTION

POSTER SESSION-PB: 3:30 P.M. Tuesday, May 22, 1979

PB-18 M. M. Thackeray,and J. Coetzer, THE ELECTRICAL CONDUCTIVITY AND CRYSTAL STRUCTURES OF POLYAMINE IODIDE/SILVER IODIDE SOLID ELECTROLYTES

PB-19 T. Wada and J. B. Wagner, Jr., TRANSIENT CURRENT IN THE CELL, ⊖ Cu |CuI| GRAPHITE ⊕

PB-20 T. Wada and J. B. Wagner, Jr., HOLE CURRENT-VOLTAGE CHARACTERISTICS IN ⊖ Cu |CuI| GRAPHITE ⊕

PB-21 B. Baranowski and A. Lunden, VOLUME OF ACTIVATION FOR FAST IONIC CONDUCTION - A PROPOSITION FOR SOLID AND MOLTEN SALTS

PB-22 A. Clearfield and P. Jirustithipong, KINETICS OF GAS-SOLID AND SOLID-SOLID REACTIONS IN ZIRCONIUM PHOSPHATE

PB-23 E. Prasad, M. Sayer and J. Corey, DETERMINATION OF DIFFUSION COEFFICIENT OF SOLID ELECTROLYTES FROM MEASUREMENTS ON POLARIZATION CELLS

PB-24 S. R. Shatynski, CHEMICAL DIFFUSION IN MULTICOMPONENT SOLIDS

PB-25 A. R. Bishop, W. Dieterich and I. Peschel, INTERACTING BROWNIAN PARTICLES IN A PERIODIC MEDIUM

PB-26 A. Bunde, STATICS AND LOCAL DYNAMICS OF SUPERIONIC CONDUCTORS NEAR THE PHASE TRANSITION

PB-27 P. M. Richards, FREQUENCY DEPENDENCE OF HOPPING CONDUCTIVITY

PB-28 E. Siegel, ORIGIN OF THE TWO-LEVEL SYSTEM IN SUPERIONIC CONDUCTORS

PB-29 D. C. Ailion and C. E. Hayes, EFFECTS OF ABSORBED WATER ON NMR LINESHAPE AND T_1 IN Na β''-ALUMINA

PB-30 J. L. Bjorkstam and M. Villa, Al^{27} NMR IN SINGLE CRYSTALS OF β-ALUMINAS

PB-31 A. Highe and R. W. Vaughan, EVALUATION OF CATION DISTRIBUTION IN Li/Na β-ALUMINA FROM FIRST-ORDER QUADRUPOLAR NMR SPECTRA

PB-32 K. L. Ngai, ac CONDUCTIVITY AND NMR RELAXATIONS IN IONIC CONDUCTORS

PB-33 A. R. Ochadlick, Jr., W. Bailey, H. S. Story, G. C. Farrington and J. Briant, PROTON MAGNETIC RESONANCE IN NH_4-β AND NH_4-β''ALUMINA

POSTER SESSION-PB: 3:30 P.M. Tuesday, May 22, 1979

PB-34 R. J. Cava, F. Reidinger and B. J. Wuensch, CONDUCTIVITY MECHANISMS IN THE SUPERIONIC PHASES OF AgI AND Ag_2S AS DETERMINED BY NEUTRON DIFFRACTION

PB-35 Y. Chabre, P. Segransan, C. Berthier, and G. Ouvrard, NMR NMR AND NEUTRON DIFFRACTION STUDIES OF MIXED CONDUCTORS $Li_x MPX_3$

PB-36 M. H. Dickens, W. Hayes, M. T. Hutchings and C. Smith, ANION DISORDER IN TWO FLUORITES AT HIGH TEMPERATURES AS DETERMINED BY NEUTRON DIFFRACTION.

PB-37 M. H. Dickens, W. Hayes, M. T. Hutchings, J. Kjems and C. Smith, INVESTIGATION OF ANION MOTION IN FLUORITES AT HIGH TEMPERATURES USING NEUTRON QUASI-ELASTIC SCATTERING

PB-38 W. F. Kuhs, and G. Heger, NEUTRON DIFFRACTION STUDY OF CU_6PS_5Br AT 293 K AND 473 K

PB-39 S. M. Shapiro and M. B. Salamon, SINGLE PARTICLE EXCITATIONS IN $RbAg_4I_5$

POSTER SESSION-PC: 8:00 P.M. Wednesday, May 23, 1979

PC-1 A. V. Chadwick, D. S. Hope, G. Jaroszkiewicz and J. H. Strange NMR AND CONDUCTIVITY STUDIES OF IONIC TRANSPORT IN LaF_3

PC-2 G. Couturier, Y. Danto, J. Pistre, J. Salardenne, C. Lucat, J. M. Reau, J. Portier and S. Vilminot, THE ANIONIC CONDUCTOR $PbSnF_4$: STUDY OF THIN FILMS AND CERAMICS

PC-3 J. M. Oberschmidt and D. Lazarus, ACTIVATION VOLUMES OF SUPERIONIC CONDUCTORS WITH THE FLUORITE STRUCTURE

PC-4 D. O. Pederson, J. A. Brewer, G. T. Chew, R. B. Foster, and S. R. Montgomery, ULTRASONICS IN IONIC CONDUCTING FLUORIDE FLUORITES

PC-5 D. Gourier and B. Sapoval, AMMONIUM IONS ARE "ROLLING" IN BETA ALUMINA

PC-6 H. Arribart, J. F. Gouyet and B. Sapoval, ORDER-DISORDER TRANSITION BETWEEN OFF-CENTER POSITIONS IN THE MIXED CONDUCTOR Cu_3VS_4

PC-7 H. Arribart and B. Sapoval, CHEMICAL ORIGIN OF THE MOBILE IONS AND NUCLEAR RELAXATION IN Cu_3VS_4

PC-8 D. S. Rimai and R. J. Sladek, PRESSURE DEPENDENCES OF THE ELASTIC CONSTANTS OF CUBIC PbF_2 AT 296 K and TEMPERATURE DEPENDENCES OF THE SPECIFIC HEAT OF CUBIC AND ORTHORHOMBIC PbF_2

PC-9 R. D. Hogg, S. P. Vernon and V. Jaccarino, MAGNETIC TAGGING OF ION DIFFUSION IN PbF_2

PC-10 G. Burns, LATTICE DYNAMICS OF BINARY SUPERIONIC CONDUCTORS

PC-11 S. W. de Leeuw and J. W. Perram, MOTION OF CHARGE CARRYING IONS IN SODIUM β-ALUMINA

PC-12 M. Dixon and M. J. Gillan, FAST ION TRANSPORT IN $SrC\ell_2$

PC-13 T. M. Hayes and J. B. Boyce, ION FLOW IN A SUPERIONIC CONDUCTOR

PC-14 W. Schommers, STRUCTURAL AND DYNAMICAL BEHAVIOR OF α-AgI

PC-15 P.W.M. Jacobs, J. Corish, B. A. Devlin and C.R.A. Catlow, IONIC TRANSPORT IN SILVER HALIDES

PC-16 J. A. Cowen, C. L. Foiles and D. L. Edmunds, THERMOPOWER MEASUREMENTS IN $RbAg_4I_5$ FILMS

POSTER SESSION-PC: 8:00 P.M. Wednesday, May 23, 1979

PC-17 J. A. Cowen and D. L. Edmunds, VISUAL OBSERVATION OF THE TRANSPORT OF SILVER THROUGH A $RbAg_4I_5$ FILM

PC-18 T. Ohachi and I. Taniguchi, GROWTH OF α-Ag_2S AND α-Ag_2Se SINGLE CRYSTALS THROUGH A CAPILLARY TUBE

PC-19 L. B. Coleman, THERMOELECTRIC POWER STUDIES OF PHASE TRANSITIONS IN FAST ION CONDUCTORS

PC-20 D. Brinkmann, W. Freudenreich, H. Looser, M. Mali and J. Roos, STATIC AND DYNAMIC NMR EFFECTS AROUND THE 209 K PHASE TRANSITION IN $RbAg_4I_5$.

PC-21 D. Brinkmann, M. Mali and J. Roos, DIFFUSION PROCESSES IN Li_3N STUDIED BY ^6Li NMR

PC-22 P. Hartwig, W. Weppner and W. Wichelhaus, FAST IONIC CONDUCTION IN SOLID LITHIUM NITRIDE HALIDES

PC-23 J. R. Walker and C.R.A. Catlow, DEFECT PROPERTIES AND IONIC TRANSPORT IN LITHIUM NITRIDE

PC-24 H. Schulz and U. Zucker, INTERSTITIAL SITES AND ANHARMONIC THERMAL VIBRATIONS IN THE CRYSTAL STRUCTURE OF LITHIUM NITRIDE (Li_3N)

PC-25 H. Guth and G. Heger, TEMPERATURE DEPENDENCE OF THE CRYSTAL STRUCTURE OF THE ONE-DIMENSIONAL Li^+-CONDUCTOR β-EUCRYPTITE ($LiAlSiO_4$)

PC-26 K. Funke, DYNAMIC CAGE EFFECT: COMPARISON BETWEEN α-$RbAg_4I_5$ AND α-AgI

PC-27 H. U. Beyeler, J. Bernasconi and S. Strassler, IONIC CONDUCTIVITY OF HOLLANDITE: A MODEL SYSTEM FOR THE TRANSPORT IN A ONE-DIMENSIONAL SYSTEM

PC-28 G. V. Chandrashekhar and S. J. La Placa, A ONE DIMENSIONAL SODIUM ION CONDUCTOR

PC-29 C. Delmas, A. Maazaz, C. Fouassier, J. M. Reau and P. Hagenmuller, IONIC CONDUCTIVITY IN SHEET OXIDES

PC-30 M. G. Shilton and A. T. Howe, EVIDENCE FOR PROTON CONDUCTIVITY IN COMPOUNDS IN THE HYDROGEN - URANYL - PERIODATE - WATER SYSTEM

PC-31 H. W. Willemsen, R. L. Armstrong and P.P.M. Meincke, PROTONIC CONDUCTION OF HYDROGEN IMPURITIES IN $K_2O_sCl_6$

POSTER SESSION-PC: 8:00 P.M. Wednesday, May 23, 1979

PC-32 J. M. Newsam and B. C. Tofield, ANHYDROUS DEUTERIUM BETA ALUMINAS

PC-33 K. K. Kim, G. V. Chandrashekhar, W. K. Chen and J. N. Mundy, TEMPERATURE DEPENDENCE OF THE HAVEN RATIO IN SILVER BETA-ALUMINA

PC-34 J. P. Boilot, G. Collin and R. Comes, MODELS FOR ION-ION CORRELATION IN β-ALUMINA COMPOUNDS

PC-35 J. P. Boilot, Ph. Colomban, G. Collin and R. Comes, X RAY STUDIES OF β AND β"-ALUMINA WITH HIGH CONDUCTION ION CONCENTRATION

PC-36 J. L. Briant and G. C. Farrington, IONIC CONDUCTIVITY IN Na^+, K^+, AND Ag^+ BETA"-ALUMINA

PC-37 A. Hooper, CHARACTERIZATION OF NH_4^+ EXCHANGED SINGLE CRYSTAL BETA-ALUMINA

PC-38 J.-O. Bovin, HIGH RESOLUTION ELECTRON MICROSCOPY STUDIES OF β- and β"-ALUMINAS

PC-39 S. R. Kurtz and H. J. Stapleton, ELECTRON SPIN RELAXATION BY TUNNELING STATES IN $Na\text{-}\beta\text{-}Al_2O_3$

ABSTRACTS

of

INVITED PAPERS

OVERVIEW OF BASIC AND APPLIED RESEARCH ON BATTERY SYSTEMS AT ARGONNE*

M. V. Nevitt, Argonne National Laboratory, 9700 S. Cass Avenue,
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This paper will point up the need for a basic understanding of the ion-transport and related effects that are observed under the unique physical and electrochemical conditions occurring in high-temperature, high-performance batteries. Such effects include those that are typical of transport in bulk materials such as liquid and solid electrolytes and the less well understood effects observed in migration in and across the interfacial zones existing around electrodes. The basic and applied studies at Argonne National Laboratory, centered in part around the development of a Li(alloy)/iron sulfide battery system for energy storage, will be briefly described as an example of the way that such an understanding is being sought by coordinated interdisciplinary research.

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* Work performed under the auspices of the U. S. Department of Energy.

ROLE OF BASIC RESEARCH IN OUR ENERGY FUTURE

James S. Kane, Associate Director for Basic Energy Sciences
Office of Energy Research

The United States finds itself in an energy situation that consists of two independent, but equally grave components.

Stated very briefly, problem number one is the increasing price of readily available (at least prior to the revolution in Iran) energy. This is causing severe economic difficulties with Americans, who refuse to live within their energy means, and to the developing world, which has insufficient means to live within.

The second problem is one of very difficult time constants. The supply of cheap and convenient fuels we now rely on is finite, and we face the very real and difficult problem of bringing on the new sources in time to permit a smooth transition from current depleting sources. Our energy system is huge, expensive and pervasive. To change it from its current reliance on gas and petroleum to the new sources will require enormous effort, and a corresponding long lead time.

All new sources of energy will be very expensive, in comparison with today's energy costs. All have very difficult technical problems. Along with this need for new sources of supply, there is the need to totally reconfigure the ways in which Americans use energy. America developed when energy was cheap; it is not surprising that we consume inefficiently. Yet redesigning the end-use part of the energy system is also a process of long time constants.

The sum of all these requirements is nothing less than a total restructuring of our energy system, and in some ways, our lives. To do this in time, and at an ultimate cost, both economic and environmental, that we can afford will challenge all parts of our society, including the scientific enterprise.

The role of basic research is to examine carefully the scientific opportunities related to the impediments to new sources, the difficulties with present ones, and inefficiencies in the ways we consume. In this talk I will review some of the more critical research needs in the different areas of technology, and illustrate benefits such research could bring.

LAYER AND TUNNEL COMPOUNDS - FAST ION TRANSPORT AND ELECTROCHEMICAL ENERGY STORAGE

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Electrochemical systems are needed for the reversible storage of electrical energy to be used in utility load leveling, electric vehicle propulsion, solar electric storage, and electronic devices. The key components in batteries that require fast ion transport in the solid state are the electrolyte and the electronegative electrode, the cathode. Characterization of these components requires a knowledge of their structure, thermodynamics and ion kinetics.

The key characteristics of solid electrolytes and cathodes will be discussed in relation to those of the layered compounds beta alumina and titanium disulfide. These will then be extended to tunnel structures such as found amongst the transition metal oxides and sulfides. Among the areas to be discussed are the effect of ionic radius and structure on ionic mobility, diffusion mechanism, topochemical and reversible cathode reactions, and the importance of thermodynamics to both components.

LITHIUM/METAL SULFIDE BATTERY DEVELOPMENT

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Lithium/metal sulfide batteries are being developed by Argonne National Laboratory and industrial contractors for electric-vehicle propulsion and for stationary-energy-storage applications such as load leveling. The battery cells consist of lithium-aluminum or lithium-silicon negative electrodes, iron sulfide (FeS or FeS_2) positive electrodes, and molten $LiCl$-KCl electrolyte. The cells are enclosed in a thermally insulated jacket to maintain an operating temperature of 400-500°C. A 40-kW-hr electric-vehicle battery consisting of 120 Li-Al/FeS cells is currently being fabricated and is scheduled for laboratory and in-vehicle testing in 1979.

SODIUM/SULPHUR TRACTION BATTERIES - A REVIEW OF PROGRESS AND PROBLEMS IN THEIR DEVELOPMENT

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Sodium/sulphur batteries based on beta alumina as solid electrolyte have been under intensive development for thirteen years. In Europe the emphasis has been on traction batteries for road vehicles and railway applications. This paper presents an overview of recent progress, particularly in the U.K., and attempts to set this in the framework of problems remaining to be solved.

Recent developments in cell design and construction are reviewed first, followed by a consideration of each of the major components in turn. The importance of materials science and technology in determining the electrical performance and durability of cells is emphasised. Causes of cell deterioration and failure in use are discussed. The overall objective of producing a cell of high energy density and low cost, which is reliable and maintains its capacity for a long life, and which is guaranteed safe in use is seen to be a formidable technical challenge. An inter-disciplinary team approach has resulted in cell designs which are well on the way to meeting this specification, although much detailed work remains to be done before success is assured.

Several battery experiments of increasing scale, up to 10 kWh, have been conducted to obtain information on the electrical behaviour of series/parallel arrays of cells. Safe operation of these batteries has been achieved by incorporating appropriate safety design features into the cells. Further development work on batteries will require the provision of large numbers of cells, and pilot plant production facilities for these are now being installed.

I-6

ADVANCED BATTERY PROGRAM IN GENERAL ELECTRIC

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Since 1973, sodium-sulfur battery development at GE, with co-sponsorship by the Electric Power Research Institute (EPRI), has been directed at the application of load leveling for utility service. The sodium-sulfur battery concept is highly attractive in this application in that non-critical materials are used and, by comparison to the lead acid battery, is five-fold more compact. At the heart of the cell is a beta-alumina solid electrolyte which acts as a barrier to the molten sodium and sulfur and only permits the passage of sodium ions during cell operation. To provide the desired high efficiency (75%), the cell operates at between 300 and 350°C. This required high temperature cell environment contributes to the many challenges facing the development of this advanced battery concept.

Between 1973 and 1977, work at GE was focused on developing the critical elements of the cell on a small, prototype scale. These critical elements included the (1) ceramic electrolyte, (2) corrosion resistant container coatings, (3) seals (interior and exterior), and (4) sulfur electrode designs. Hundreds of small cells (16 AH) have been tested for life and performance in the development of these cell elements. Typical life of these small cells now exceed 700 cycles. The primary failure mode has been the mechanical exterior seal which has recently been replaced by a novel thermocompression bond with long-life potential.

The success of small laboratory cells has provided the confidence for scaling up the cell to a commercial prototype size (full size). This full-size cell has been designed with a ten-fold increase in capacity to 160 AH. The critical scale-up development is now complete. Electrical performance testing of full-size cells began in January of 1979, following a six-month period of safety evaluation testing. To date, these cells have performed satisfactorily meeting the design depth of discharge (80% of theoretical).

In parallel with this effort, a system design has been undertaken for packaging cell groups. The result of this work has been the development of a 100 Kwh liquid-cooled module. Such a module contains 360 cells in electrical parallel-series connection. The liquid-cooled cathode busbar acts to provide both the cell heat transfer and current collection. A sub-module, called a bundle, consisting of 20 full-size cells in parallel, will be under test by June as a major demonstration of this advanced battery concept.

Details of the cell scale-up and testing are the subject of this paper. The solid ceramic electrolyte development will be given special emphasis.

PRECISION ANALYSIS OF THE Li/TiS_2 BATTERY

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Detailed measurements on the Li/TiS_2 battery couple have revealed subtleties on the voltage composition relation that are related to the structural ordering of lithium ions intercalated into TiS_2.[1] The impact of these results on our understanding of intercalation chemistry and on battery operation will be discussed. Recent measurements on other cathode materials will be compared to TiS_2.

[1] A. H. Thompson, Phys. Rev. Lett., 40, 1511 (1978).

I-8

EVALUATION OF PROPERTIES RELATED TO THE APPLICATION OF FAST IONIC TRANSPORT IN SOLID ELECTROLYTES AND MIXED CONDUCTORS

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Recent work on materials exhibiting fast ionic transport has led to the possibility of a wide range of practical applications. These fall into two general classes. In one of these, the critical feature is the selective transport of ionic species in solids which are essentially electronic insulators, so they can be used as solid electrolytes. In the other the existence of mixed conduction, with both rapid ionic transport and appreciable electronic conductivity, is important.

In solid electrolytes, initial attention is generally focused upon the questions of the magnitude of the ionic conductivity and the ionic transference number. However, their practical utilization is often seriously limited by other factors. Important among these are the restricted ranges of chemical potentials over which they are thermodynamically stable and over which they conduct electric charge primarily by ionic transport. Techniques will be discussed whereby these features can be evaluated.

The practical utilization of mixed conductors often also involves the evaluation of the ranges of chemical potential and composition over which specific phases can exist. Especially interesting for some applications are materials which undergo insertion reactions in which appreciable concentrations of certain relatively mobile ionic species can be accommodated within essentially static host crystal lattices. In this case one of the other important parameters, which controls the rate of the insertion process, is the chemical diffusion coefficient. It has recently been demonstrated that several techniques involving the use of galvanic cells can be employed to evaluate chemical diffusion in intermetallic compounds and other mixed conductors, such as ternary oxides and chalcogenides. These will be discussed, and it will be shown that, when used in conjunction with coulometric titration, such techniques can also provide high compositional resolution in phases with narrow composition ranges.

AMBIENT TEMPERATURE SOLID STATE BATTERIES

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Conceptually, ambient temperature solid electrolytes would permit the design of batteries exhibiting enhanced operating characteristics over a wide temperature range and minimal parasitic losses.

Most of the development effort has been expended on primary batteries based upon the Ag/I_2 and Li/I_2 couples. However, a major limitation has been the inherent restriction to very low power or energy densities. Cells utilizing the solid electrolyte $RbAg_4I_5$ ($\sigma=0.28\Omega^{-1}cm^{-1}$) have current capabilities in the mA/cm^2 range and energy densities limited to $<0.1Wh/cm^3$ by the decomposition EMF and the use of silver anodes.

Li cells based upon LiI or $LiI(Al_2O_3)$ exhibit a marked increase in energy density at very low power levels, and are expected to deliver 0.8Wh/cc in cardiac pacemakers. The requirement of 80μW average power drain for five to ten years, under isothermal (37°C) conditions has been effectively met by solid state batteries. Further improvements in this area of battery technology will result from solid electrolyte materials that simultaneously exhibit fast ion conductivity, high decomposition potentials and compatibility with rechargeable electrode materials.

I-10

NEW TYPES OF SOLIDE ELECTROLYTE GAS SENSORS

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The current status of the conventional sensors is reviewed. The various types of reference electrode and typical applications are described.

Two new possibilities were investigated. One involved a contact between two solid electrolytes either identical or different in composition. Such a contact can eliminate the most detrimental effect of the internal electronic short circuit. It can also make the sensor more specific for complex gas analysis.

The second is based on the utilization of a supported electrolyte. Experimental results obtained with $SrCl_2$ - based solid solutions illustrate this possibility and shows that working temperature of the oxygen gauge can be significantly lowered in this way.

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*Presently at the University of California, Santa Barbara.

ELECTROCHROMISM OF ANODIC IRIDIUM OXIDE FILMS (AIROFs)

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We review the preparation and properties of a new electrochromic material, an anodically-grown Iridium Oxide film (AIROF) and discuss the mechanism of its electrochromic process. The AIROFs' main characteristics are: fast coloring and bleaching times; good contrast in reflection and transmission; good open circuit memory and stability; long lifetimes in operation; low switching voltage and power consumption; no major side reactions; operability at room temperature; insensitivity to temperature fluctuations, and relatively sharp threshold.

We describe the major recent developments in AIROFs' electrochromism, i.e. 1) a heat treatment which improves response times and greatly improves stability; 2) the observation that the maximum coloration and the speed of response are independent of pH, i.e. essentially the same for acidic, neutral, or alkaline electrolytes, 3) a transmission cell in which the AIROF is grown on a semi-transparent conducting substrate, and 4) all solid state electrochromic cells based on solid electrolytes.

We also describe the observation of a new electrochromic isotherm in AIROFs, and show that there are two distinct electrochromic processes with different isotherms. Both isotherms are dominated by internal entropy changes of non-interacting particles and are quantitatively different from those of proton injection processes in WO_3 electrochromics. These results indicate that AIROFs are ideal entropy batteries and that processes other than simple proton injection can charge (color) and discharge (bleach) them.

ORDERING OF THE CONDUCTING IONS IN SILVER β ALUMINA

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X-ray scattering investigations of silver β alumina (11 Al_2O_3 - x Ag_2O with $0.3 < x < 1$) reveals at low temperature an ordering of the conducting ions which is markedly stoichiometry dependent. While the high temperature conducting state of the conducting ions can be shown to be always characterized by a 2D quasi-liquid order, at low temperature a progressive quasi crystalling order is found to build up. For the nonstoichiometric crystals, this order is a short range superstructure. For stoichiometric crystals ($x \simeq 1$) on contrary, a similar type of ordering is found but is long range, and a clear phase transition is observed between the high temperature conducting state and the low temperature nonconducting phase.

NEUTRON DIFFRACTION STUDIES OF BETA ALUMINAS AND OTHER IONIC CONDUCTORS

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J.M. Newsam, Chemical Crystallography Lab, Parks Road, Oxford, England

We have been interested to understand structural features influencing fast ion conductivity in oxyacid salts and in beta aluminas. Of particular interest have been beta aluminas substituted with hydrogen, which are stable to water loss to quite high temperatures, and are promising prototype materials for proton conducting electrolytes in atom monitors or electrical power devices.

The chemistry of beta alumina with sodium substituted by protons in different ways, as documented in the literature, is confusing and complicated. Various materials have been studied using neutron and x-ray diffraction as part of an attempt to understand this chemistry. Anhydrous polycrystalline deuterium beta aluminas prepared from silver precursors have a D-O(5) bond at low temperature, the normal site occupied by cations being empty, and a stoichiometric composition, $DAl_{11}O_{17}$. There are, however, structural variations from material to material, and with temperature.

Ammonium beta alumina single crystals, prepared by exchange for sodium in ammonium nitrate, have been studied at room temperature by x-ray and neutron diffraction, and, after high temperature treatment to remove ammonia, by neutron diffraction. Preliminary refinements show NH_4^+ ions to be centred at the Beevers-Ross position with the proton positions revealed. Additional scattering intensity near mid-oxygen sites may indicate the presence of water as well as NH_4^+ in the mirror plane. After treatment at 600°C or above, but without exposure to moisture, a different material is obtained to that prepared by direct hydrogenation of silver beta alumina.

STRUCTURE INVESTIGATIONS OF SUPERIONIC CONDUCTORS: REQUIREMENTS, RESULTS AND NEW QUESTIONS.

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Disorder on the sublattice of mobile ions can be caused by defects in the framework structure, as in the β-aluminas, by a thermally induced transition, e.g. the fluorites, or is inherent in the particular structure, as in α-AgI. Structural studies of representative compounds will be discussed, with emphasis on characteristic features and implications for models predicted from theory or derived from less direct experimental techniques. The topics include: i) The relation between spinel and β-alumina, highlighted by the recognition that both $1.22Na_2O \cdot 11Al_2O_3$ and $Na_{1.66}Mg_{.66}Al_{10.33}O_{17}$ are stabilized by the expulsion of 2/3 of a positive charge from a spinel block. ii) Comments on coordination and bonding characteristics, in particular the similarity between the Strock model for α-AgI and the superionic fluorite phase. iii) Relations between pair potential, site potential, probability density and diffusion mechanism as found in α-AgI and the isostructural V, Nb and Ta hydrides. These compounds permit the independent measurement of frequencies and corresponding mean square displacements of oscillators in the classical and quantum limit respectively. There is strong evidence that the equipartition theorem may be valid even for the latter, in contradiction to the universally accepted model.

Repeatedly, the danger of substituting 'reasonableness' for experimental facts will be demonstrated, but above all, the need for closer cooperation between scientists using different techniques will become apparent.

EFFECT OF PRESSURE AND COMPOSITION ON FAST Na^+-ION TRANSPORT IN THE SYSTEM $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$*

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Very high Na^+-ion conductivities have been observed in the system $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$.[1] For example, the conductivity of NASICON ($Na_3Zr_2PSi_2O_{12}$) is 0.4 Ω^{-1} cm^{-1} at 300°C, equaling the value for high-grade Na-β-alumina ceramics. In addition, longevity tests have shown that NASICON exhibits considerable stability in the presence of molten Na and Na_2S_x. The materials in the $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ system are solid solutions varying continuously in composition over the range $0 \leq x \leq 3$, with a structure consisting of a three-dimensional network of SiO_4 and/or PO_4 tetrahedra corner-shared with ZrO_6 octahedra. The mobile Na^+ ions partially occupy the three-dimensionally connected interstitial space formed by the alternatingly linked tetrahedra and octahedra. We have measured the effect of hydrostatic pressure (to 7 kbar) and composition on ionic conductivity for a series of ceramic specimens with densities exceeding 95% of theoretical. The conductivity decreases with pressure, with a dependence corresponding to a positive activation volume. This volume decreases as x increases, indicating an increase in bottleneck size with increasing x. This change is consistent with the effect of composition on conductivity, which exhibits a broad maximum for x of 1.8 to 2.4, increasing slightly as x increases over this range although the concentration of vacant Na^+ positions decreases by 50%.

*This work was sponsored by the Department of Energy.

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[1] J. B. Goodenough, H. Y-P. Hong, and J. A. Kafalas, Mater. Res. Bull. 11, 203 (1976).

NEUTRON DIFFRACTION OF DOPED Bi_2O_3 and Li_4 SiO_4 AND RELATED STUDIES

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Powder neutron diffraction studies provide an important first step in the determination of the structure of many fast ion conductors. The advantages and disadvantages of powder techniques for the structural investigation of these materials is discussed with particular reference to results obtained for SrO doped Bi_2O_3 and for $Li_{4-x}P_xSi_{1-x}O_4$ and $Li_{4-2x}S_xSi_{1-x}O_4$. The impact of some of the future developments in both neutron single crystal and powder techniques for the study of disordered solids is assessed.

FACTORS AFFECTING ION MOBILITY IN SUBSTITUTION - INTERCALATION COMPOUNDS IN CHALCOGENIDE HOSTS

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The A_xMS_2 intercalation compounds of alkali metals in lamellar dichalcogenides are generally both electronic and ionic conductors. The ionic conductivity is related to the diffusion of the Na^+ ions between the slabs of the host. At the same time intercalation in semi-conducting chalcogenides (ZrS_2, HfS_2 for example) induces an electronic contribution which results from the ionization of the A atoms, each of them being supposed to give one electron to the conduction band.

It is possible to suppress this induced electronic contribution by performing simultaneously a substitution in the slab and an intercalation between them. The $A_xM'^{III}_xM^{IV}_{1-x}S_2$ derivatives (M' = In, Y ..., M^{IV} = Zr, Hf, Sn ..., $0 < x \leqslant 1$) are valuable ionic conductors. They provide good models for studying ionic mobility in a true two-dimensional space according to the various structural types, the values of x, the nature of the M' and M cations. An experimental study has been carried out according to these factors.

In a given series of compounds the activation energy strongly depends on the ratio of the occupied and available sites in the Van der Waals gap. Concerning the covalency of the host structure it is found that the greater the fractional ionicity of the M-S and M'-S bonds, the higher the activation energy. For the alkali metal ions trigonal prismatic sites are also more favorable than octahedral sites for ionic mobility. The relationship between these factors are discussed and interpretations are proposed.

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* Associated to CNRS (L.A. N° 279).

I-18

POLY-ETHERS AS SOLID ELECTROLYTES

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We have investigated the complexes formed by poly (ethylene oxide) (PEO) and poly(propylene oxide) (PPO) and alkali metal salts as cation transducers.

PEO has strong solvating properties and gives adducts with selected salts of the five alkali-metals, however, with the lighter elements (Li,Na), the complexes formed are crystalline; the polymeric solid electrolytes thus formed are tough materials, with thermoplastic properties.

PPO, on the other hand, has excellent elastomeric properties, with a low Tg (-60°C) the low crystallinity due to the steric hindrance of the pendant methyl group, for material obtained by non-stereospecific polymerisation procedures. With less pronounced solvating properties, PPO forms complexes only with Li and Na salts of the strongest acids (HSO_3CF_3,$HClO_4$). The adducts retain the elastomeric properties of the salt-free polymer with even improved tensile strengh.

The conductivity of these solid electrolytes is strongly dependant on salt concentration (O/M ratio). Optimization of composition leads to materials with the desired mechanical properties and conductivities $> 10^{-5}$ $(\Omega \, cm)^{-1}$ at low temperature (40°C).

TOPOCHEMICAL REACTIONS OF METAL OXIDES WITH LITHIUM

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Two large classes of transition metal oxides with framework structures have been found to reversibly incorporate lithium at room temperature. One class consists of the rutile related dioxides, MO_2. In order for lithium incorporation to proceed at moderate rates the rutile must have a relatively large unit cell and metallic conductivity. The other class consists of compounds having perovskite related lattices with vacant A sites, such as ReO_3 and the shear related vanadium oxides V_2O_5, V_6O_{13}, and $VO_2(B)$. The prototype ReO_3 reversibly accommodates 2.3 lithium ions per perovskite cavity. For the vanadium oxides, the V_2O_5 lattice can accommodate only one lithium ion per cavity before irreversible structural changes occur, whereas the V_6O_{13} and $VO_2(B)$ lattices can incorporate approximately four lithium ions per cavity without irreversible structural changes. For V_6O_{13} this results in an overall stoichiometry of $Li_8V_6O_{13}$. The cells $Li/Li^+/V_6O_{13}$ have excellent rechargeability in the voltage range of 2.8-2.2 volts. The theoretical energy density is 800 Whr/Kg.

The chemical preparation and characterization of the various new ternary oxides will be discussed. All the ternary oxides of interest are unstable at elevated temperatures ranging from 80°C (for $LiWO_2$) to 300°C (for LiV_2O_5).

HIGH ALKALI ION CONDUCTIVITY IN RAPIDLY QUENCHED OXIDES CONTAINING NO NETWORK FORMERS

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Non-crystalline solids would appear to be well suited for applications as solid electrolytes. The materials are characterized by the high degree of structural disorder required for fast ion transport and they can be prepared with a high density of mobile ion species. In addition they have isotropic ionic conductivity and a lower electronic conductivity than their crystalline counterparts.

We have prepared a large variety of new oxide glasses containing no network forming additives, by twin-roller quenching. The majority of glasses do not devitrify below 400°C. In all the cases we have studied, the glasses exhibit ionic conductivities considerably greater than crystalline materials of the same composition. Room temperature lithium ion conductivities up to 10^{-5} ohm^{-1} cm^{-1} have been measured in Niobate and Tantalate glasses, which have crystalline conductivities below 10^{-20} ohm^{-1} cm^{-1}.We will report a systematic study of over 100 glass compositions in which we have observed the effects of cation radius, fractional alkali ion content of the glass and mixed alkali effects. We will also report preliminary measurements on the more conductive glasses prepared by sputtering techniques.

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DIFFUSION AND IONIC CONDUCTIVITY IN SOLID ELECTROLYTES*

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In ionic solids, the most usual experimental method of determining the correlation factor (f) has been a comparison of tracer diffusion and ionic conductivity. Theoretical values of f have been determined for many lattice geometries and jump processes and compared with measured values of f as a means of determining the atomic jump process. This paper considers the problems of applying this technique to solid electrolytes where the concentration of defects responsible for diffusion is comparable to the concentration of the mobile ions. The present level of theoretical understanding will be outlined and the difficulties of applying the more common experimental techniques for the study of f to solid electrolytes will be discussed.

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FAST ION CONDUCTING GALLATES AND ALUMINATES--
SIMILARITIES AND DIFFERENCES

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The gallium analogs of β and β"-alumina exist and are themselves excellent fast ion conductors. Study of both of these systems together provides a means of investigating the effect of certain property changes on the performance of the materials. The principal difference between the gallates and aluminates are the higher sodium contents of the former, and the different way in which the charge of the excess sodium is compensated. Moreover, β"-Na-gallate can be grown as a pure monocrystal, whereas β"-Al_2O_3 must be stabilized with Mg or Li. A typical composition for β-Na-gallate is $Na_2O \cdot 6.9Ga_2O_3$, and for β" $Na_2O \cdot 5.9Ga_2O_3$. About 10% of the sodium in β-gallate and 14% in β" is non-mobile and is thought to substitute for Ga in the spinel block. Evidence is presented that this substitution provides the charge compensation for the excess interstitial sodium in the conduction plane.

DC conductivities at 300°C of 1.02 $(\text{ohm-cm})^{-1}$ for β"-Na-gallate, and .37 and .215 $(\text{ohm-cm})^{-1}$ for β-Na-gallate and β-Al_2O_3, respectively, have been measured. However, the conductivity is found to be very composition dependent with up to 8-fold variation observed with about 5% change in sodium content. This dependence is not predicted by present diffusion theories. The identity and concentration of the actual charge carriers will be discussed.

Both gallates and aluminates exhibit the "mixed alkali effect", a strong maximum in activation energy for conduction when two different alkali ions are present. The effect is most pronounced in β-gallate.

STUDIES OF IONIC MOTION IN MIXED Na-Li β-ALUMINA

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The motion of diffusing ions in β-alumina crystals containing mixtures* of Na^+ and Li^+ has been investigated by means of ^7Li and ^{23}Na NMR studies as well as by acoustic loss measurements. Samples were prepared by exchanging flux-grown Na β-alumina crystals in melts of $LiNO_3$, with the main investigations focussed on a composition of 70% Li, 30% Na and on fully exchanged Li β-alumina. Studies of the nuclear spin-lattice relaxation rate T_1 show (a) the presence of Na^+ ions in the conduction plane has a strong effect on the diffusion properties of the Li^+ ions, (b) the Na^+ ions are less strongly affected by the Li^+, thus are not "stationary" as found in ceramic material of similar composition by Farrington and Roth*, and (c) further strong changes in the ^7Li T_1 and quadrupole splitting are effected by heat treatment to 700°C for 1/2 hour. These observations are supported by acoustic loss spectra.

Acoustic loss measurements on Na β-alumina also lead to a rather direct deduction of activation energy and prefactor for Na^+ ion motion, giving results for the attempt frequency in agreement with infrared spectroscopic values. Thus the prefactor anomaly noted earlier† will need to be resolved by a modified interpretation of the NMR results.†

*W. Roth and G. C. Farrington, Science 196, 1332 (1977).

†R. E. Walstedt, R. Dupree, J. P. Remeika and A. Rodriguez, Phys. Rev. B 15, 3442 (1977).

I-24

IONIC TRANSPORT IN SOME FLUORITE-STRUCTURED SOLID SOLUTIONS

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The alkaline earth fluorides and cubic lead fluoride (MF_2) form extended fluorite-structured solid solutions with trivalent (MeF_3) and tetravalent ($Me'F_4$) metal fluorides. The isothermal ionic conductivity of the anion-excess solid solutions $M_{1-x}Me_xF_{2+x}$ and $M_{1-x}Me'_xF_{2+2x}$ increases more rapidly than linearly with solute content over wide ranges of x.[1,2] A review is presented of recent results of this unusual compositional dependence of ionic conductivity. The discussion will be focussed on the mechanism of conduction by fluoride ions. The solutes form defect clusters, and it will be shown that the superlinear increase of the ionic conductivity can be accounted for by a small fraction of highly mobile fluoride interstitials. The Enhanced Ionic Motion-model is based on interactions between the interstitials and the defect clusters.[2]

At high temperatures these fluorites go through a diffuse transition, which is characterized by the occurrence of a negative deviation from the Arrhenius relation. It will be shown that the concept of a molten anion sub-lattice beyond this transition is not appropriate. Large defect mobilities, rather than a large extent of disorder, produce ionic conductivities of the order of molten salts. At the transition temperatures the anion vacancy mobility is the same in these fluorites.

[1] J. M. Réau, J. Portier; Fluorine Ion Conductors. In "Solid Electrolytes". Eds. P. Hagenmuller, W. van Gool, Academic Press 1978, 313-333.

[2] K.E.D. Wapenaar, J. Schoonman; J. Electrochem. Soc. 126 667 (1979).

NEW SOLID ELECTROLYTES WITH HIGH IONIC CONDUCTIVITY*

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Two types of materials have been investigated :

1) Ternary fluorides with cations of high polarizability and structure derived from the CaF_2-type.

The best material so far studied is $PbSnF_4$, which has a conductivity close to $10^{-1}\Omega^{-1}cm^{-1}$ at 150°C and an activation energy of 0.14eV above 80°C. The presence of cation lone pairs seems to increase strongly the mobility of the F^- ions.

2) Lithium glasses with composition B_2O_3 - xLi_2O - $yLiX$, where X is a halogen. Conductivities up to $10^{-3}\Omega^{-1}cm^{-1}$ at 150°C are obtained. They are discussed as a function of short range ordering.

The main techniques used are X-ray and neutron diffraction, complex impedance measurements, NMR studies on ^{19}F, ^{7}Li and ^{11}B, IR and Raman spectroscopies.

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*Supported by DRET.

I-26

NEUTRON SPECTROSCOPY OF FAST HYDROGEN DIFFUSION IN BCC TRANSITION METALS*

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Quasielastic neutron scattering reveals microscopic details of both the time and space development of the H-diffusion process on an atomic scale. After outlining the method on the example of PdH_x, new results on the jump geometry in bcc metals are surveyed. In particular, the anomalous diffusion behavior of H in Nb, Ta, and V at elevated temperature is emphasized, where correlated jump processes are important. The influence of impurities on the H-diffusion process is demonstrated by experiments performed on NbH_x doped with nitrogen impurities, which act as trapping centers for the diffusing hydrogen. The results are discussed in terms of a two-state random walk model which includes multiple trapping and detrapping processes. The concentration and temperature dependence of the capture and escape rates of traps are obtained.

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[†] On leave from IFF-KFA-Jülich, Jülich, West Germany.

I-27

dup

THE LOW-ENERGY EXCITATION SPECTRA OF Li, Na, K and Ag β-ALUMINA*

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Low-temperature measurements have disclosed that M-β alumina contains a broad spectrum of localized excitations ranging in energy from at least 0.03 cm^{-1} to 30 cm^{-1} and having a density of, roughly, 0.1/unit cell. It has been determined that the M ions are involved, and hence the excitations are constrained to the conducting planes. Atomic motion associated with an excitation occurs only in a direction perpendicular to the crystalline c-axis with the exception of Li β-alumina, in which motion also occurs parallel to the c-axis. The excitations appear to be similar to those found in amorphous materials, and thus may originate in the disorder characteristic of the conducting planes in β-alumina. The excitations probably arise from configurational changes accomodated by quantum-mechanical tunneling of M ions.

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I-28

THEORY OF MICROWAVE CONDUCTIVITY IN SUPERIONIC CONDUCTORS

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We study the frequency dependent conductivity $\sigma(\omega)$ for ω comparable to the jump rate Γ_o. The most general model based on pure hopping diffusion predicts a $\sigma(\omega)$ that monotonically increases from $\sigma(o)$ to an asymptotic value $\sigma(\infty)$. This behavior is consistent with experiments for β-Al_2O_3 but qualitatively at odds for Ag^+ and Cu^+ conductors. We consider therefore the effects of the dynamical processes that are beyond the simple hopping model. They are:

(a) Non thermalization of the reaction coordinate after a jump has occurred.

(b) Coupling of the jump rate Γ to an external variable such as a long lived, low frequency lattice mode.

The first of these mechanisms can give rise in principle to quasi free propagation of the reaction coordinate (soliton motion). But for most cases the large damping should prevent this situation to occurr.

The second mechanism can produce structure in $\sigma(\omega)$ of the form observed in Ag^+ and Cu^+ conductors and is supported by the experimental observations of low frequency long lived local modes.

dup

MOLECULAR DYNAMICS STUDIES OF SUPERIONIC CONDUCTORS*

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Over the last fifteen years computer modeling of liquids and solids has become a useful method of understanding the structural and dynamical correlations in these systems. This presentation will focus on some of the charcteristics of the method itself with examples taken in part from the study of liquid Lennard-Jones and alkali metals; recent work on homogeneous nucleation in monatomic liquids will be presented. This work shows that in monatomic liquids the interaction potential plays a key role in determining certain structural properties of the system; for example a Lennard-Jones system nucleates a close packed structure while an alkali metal potential nucleates a bcc packing.

In the study of ionic systems like CaF_2 the Coulomb interaction together with the short range repulsion is enough to produce a satisfactory model for the motion of F^- ions in CaF_2 at ~ 1600 K, i.e., near its melting point. A detailed analysis of this motion shows that F^- ions reside at their fluorite sites for about 6×10^{-12} s and that the diffusion is mainly a consequence of F^- jumps in the 100 direction in the lattice. The motion can be analysed in terms of the generation and annihilation of anti-Frenkel pairs.

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*Work performed under the auspices of the U.S. Department of Energy.

NMR STUDIES OF SOLID ELECTROLYTES AND SOLID SOLUTION ELECTRODES

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The contribution of NMR to a better understanding of superionic conductors is reviewed. Applications of the technique such as determination of activation energies of mobile ions, jump frequencies, self diffusion coefficients or site symmetry from quadrupolar coupling will be considered.

Particular attention will be paid to the specific problems widely encountered in the interpretation of NMR data in superionic conductors: influence of local motions on nuclear relaxation times, existence of several types of nuclei having strongly different mobilities while belonging to the same chemical species, apparent activation energy of the same order of magnitude as the measurement temperatures, anomalous prefactors of the jump frequencies and effect of the dimensionality on the pair correlation function.

Most of the illustrations will be taken from data on lamellar mixed conductors in which NMR allows a microscopic study of ion dynamics and of the modifications to the electronic properties of the host matrix.

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HYDRODYNAMICS OF SUPERIONIC CONDUCTORS

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We present a rigorous hydrodynamic theory for the collective excitations in superionic conductors at low frequencies and long wavelengths. The quantities appearing in the theory are static susceptibilities such as isothermal and adiabatic elastic constants, specific heat etc. and transport coefficients such as viscosity, electric and heat conductivities and the thermopower. Explicit expressions for the dispersion and the damping of the modes and for the density correlation are worked out for high-symmetry directions and numerically evaluated for α-AgI. In particular we show that there are two non-propagating modes. One is due to energy fluctuations and gives rise to a small central component (width $\sim k^2$, constant intensity) in scattering spectra. The other one is due to the collective diffusion of particles and causes a broad central component (width constant for $\vec{k} \to o$, intensity $\sim \vec{k}^2$) in scattering spectra. Extrapolating the theory to larger wave vectors we offer a new quantitative explanation for recent neutron scattering spectra in α-AgI. We compare the present approach also with older and less complete hydrodynamic theories and comment on the range of validity of the hydrodynamic description.

In^+ AND Tl^+ TRANSPORT IN HALIDE LATTICES

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Raman line broadening, which is sensitive to the onset of ion disorder, was employed to screen potential heavy metal halide conductors. Ionic conductivity was found to predominate in the high temperature phases of In_2ZnI_4,[1] Tl_2ZnI_4,[1] Tl_2ZnBr_4, In_2CdI_6,[1] Ag_2ZnI_4 and Ag_2CdBr_4. Comparison of order-disorder transition temperatures, conductivities, and activation energies for ion transport demonstrate that the $d^{10}s^2$ ions, In^+ and Tl^+, are less mobile than the d^{10} ions Cu^+ and Ag^+, in similar compounds. The origin of the high mobility for d^{10} ions is attributed to their ready quadrupolar polarizability which is compatible with simple crystal structures and ready passage through 3-fold halide bottlenecks.[2] By contrast $d^{10}s^2$ ions are more susceptible to dipolar polarization which leads to complex structures and higher activation energies for passage through 3-fold or 4-fold halide arrays. These ideas are compatible with structural data and with Hartree-Fock LCAOMO calculations.

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1. R. L. Ammlung, D. F. Shriver, M. Kamimoto and D. H. Whitmore, J. Solid State Chem., 21, 185 (1977).
2. W. G. Kleppmann and H. Bilz, Commun. Phys., 1, 105 (1976).

RECENT DEVELOPMENT IN SOLID SILVER AND COPPER ION CONDUCTOR MATERIALS

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Solid silver and copper ion conductors are of importance as ion conducting materials capable of using practically at room temperature.

Solid silver ion conductors have mainly been developed by introducing a certain inorganic or organic ion into the lattice of silver iodide. Recent efforts on high conductivity silver ion conductors seem to have been concentrated on the physical investigation to clarify their conduction mechanisms and on the search for developing their practical applications. In order to explain high silver ion conductivities of these conductors, various ion hopping models have been proposed, and these solid silver ion conductors have been applied to the electrolyte for solid state batteries, electrochemical functional elements and electrochromic displays.

Solid copper ion conductors have also been synthesized by incorporating some inorganic or organic ions into the lattice of copper(I) halides. Recent investigations on high conductivity solid copper ion conductors have yet been at an early stage in the development. Quite recently, copper(I) rubidium chloroiodide has been found to have a copper ion conductivity of 0.34 $\Omega^{-1}cm^{-1}$ at 25°C which is the highest ionic conductivity ever found in the solid state at room temperature and its practical application is expected to be promising.

I-34

NATURE OF IONIC MOTION IN AgI and CuI*

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Using a potential scheme based on simple motions of ionic size (and with crystal structure, cohesive energy and bulk modulous as input for determining the potential function), the nature of ionic motions has been studied with the molecular dynamics technique. The results for the temperature dependence of the diffusions constant of Ag^+ and of the mean square displacement of I^- agrees well with the experiment. The Ag^+ motion occurs between the tetrahedral sites of the I^- (bcc) lattice along rather narrow channels.+

Dynamics of the ionic motions has also been studied in γ and α phases of CuI by molecular dynamics technique using the same potential function scheme as was used for AgI. It is found that at 700 K the Cu^+ ions undergo an order-disorder transformation leading to a specific heat anomaly. The nature of the first order transition, the pair correlation functions below and above the transitions and Cu^+ density map in the unit cell will be presented.

+ P. Vashishta and A. Rahman, Phys. Rev. Lett. 40, 1337 (1978)

*Work supported by the U.S. Department of Energy.

RAMAN, INFRARED, NEUTRON DIFFRACTION AND IONIC CONDUCTIVITY STUDIES OF BETA"-ALUMINAS*

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Large single crystals of sodium beta"-alumina were grown by slow evaporation of Na_2O at 1700°C from a mixture of Na_2CO_3, MgO, and Al_2O_3 contained in a covered platinum crucible. A chemical analysis for Na, Mg, and Al gave the composition $0.8\ Na_2O \cdot 0.6\ MgO \cdot 5\ Al_2O_3$. From the neutron structure determination of a Agβ" single crystal, the composition was found to be $0.78\ Ag_2O \cdot 0.66\ MgO \cdot 5\ Al_2O_3$. Polarized Raman and infrared measurements were made on the Naβ" single crystals and on single crystals of Li, K, Rb, and Agβ" prepared by ion exchange of Naβ". The low frequency Raman spectra of Na, K, Rb, and Agβ" contained four or more bands due to vibrations of the mobile cations. These results were analyzed by assuming the spectra to be due to the normal modes of a defect cluster consisting of a cation vacancy surrounded by three cations. From model calculations, the Raman band of Naβ" at 33 cm^{-1} is assigned to the attempt mode for diffusion of Na^+ ions. Ionic conductivity measurements of Naβ" were made using a pulsed technique. The graph of log σT vs 1/T was linear and gave an activation energy for Na^+ ion conduction of 0.18 eV.

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+Guest scientist on leave from Fuji Photo Film Co., Tokyo, Japan.

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EXAFS INVESTIGATION OF SUPERIONIC CONDUCTION

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In the absence of any detailed knowledge of the paths taken by the conducting ions, models for superionic conduction have been based on either hypothetical conduction paths or general considerations like residence and hopping times. In the superionic phase, elementary considerations of mass and temperature suggest that the mobile ions spend a significant fraction of time in flight from one location to another. Therefore, structural studies can yield substantial information not only on the sites that are occupied, but also on the flight path from one site to another. The extended X-ray absorption fine structure (EXAFS) is particularly well suited to determining the conduction path since it reveals the location of the mobile ions relative to the immobile ion lattice. Since EXAFS arises from the scattering by the near neighbors of the excited atom species only, a given measurement involves only a subset of the three or more pair correlation functions probed in a single diffraction measurement.

An excluded volume model is applied to interpret the EXAFS structural data on AgI and the cuprous halides. This model approximates the cation-anion pair potential by a softened hard-sphere repulsion. Such a potential yields cation-anion pair correlation functions which are in excellent quantitative agreement with the pair correlations derived from the EXAFS measurements. In addition, this model yields information on the ionic conduction path. In BCC α-AgI the Ag ions move among the equivalent tetrahedral sites passing through the shared tetrahedral faces. In FCC α-CuI the Cu ions move through alternating tetrahedral and octahedral sites passing through the shared faces. At low temperature, the opening in the tetrahedral faces in these materials is small, confining the ions to these sites and yielding low ionic conductivity. In the superionic phase, these openings are large enough to allow the mobile ions to pass readily through the faces and yield the large ionic conductivity.

THE ROLE OF CORRELATED MOTION IN SUPERIONIC CONDUCTORS

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A central question in the physics of superionic conductors is which factors lead to an optimized ionic conductivity. Among these, the role of correlations has been investigated mainly in discrete (hopping and lattice gas) models. Qualitatively new results are expected and found when the continuous motion between the sites is taken into account. This is because the success of a motion over a potential barrier is controlled by the interactions at the barrier rather than by the interactions at the sites.

The role of correlated motion was investigated in general in a continous model which treats the ions as Brownian particles[1] with interactions of the Frenkel-Kontorova type. The conductivity is enhanced or inhibited by the correlations depending on the concentration of mobile ions. Enhancement is found when the correlations compete with the restoring forces of the cage potential. The dependence of the conductivity on the interaction strength and correlation length is reported.

The relevance of the theory for concrete superionic conductors is discussed. The possibility of soliton-like motion can be ruled out for the conductors known so far from a consideration of microscopic parameters. The most direct application of the model is for one-dimensional conductors where it predicts a maximum of the conductivity for a concentration of ~0.7 ions per potential well. The model parameters can be determined from diffuse X-ray scattering. The role of correlated motion, enhancement of the conductivity and correlation lengths are thus analyzed quantitatively for K-Hollandite.

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[1] T. Geisel, in *Physics of Superionic Conductors*, ed. M. B. Salamon (Springer, Berlin, Heidelberg, New York), Chapt. 8, to be published.

LOW FREQUENCY LIGHT SCATTERING FROM THE CUPROUS HALIDES

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The light scattering spectra of liquids exhibit scattering intensity centered at zero frequency shift which is due to the diffusive motions of the molecules. Similarly, the light scattering spectra of solids which have high ionic mobilities may be expected to yield low frequency quasi-elastic scattering due to the ionic motions. The low frequency (~2 to ~50 cm^{-1}) light scattering spectra of the cuprous halides CuI, CuBr and CuCl in the highly conducting solid and melt phases have been measured. In each case the spectra can be described by two depolarized Lorentzian components centered at zero frequency. The width of the narrow component varies from ~2 to 8 cm^{-1} while that of the broader feature is between 25 and 50 cm^{-1}. The narrow component is interpreted in terms of the fluctuations of the local atomic configurations of the mobile ions. Analogies are made between the spectra reported here and those due to density fluctuations, collision induced scattering and rotational fluctuations of anisotropic molecules in continuous or liquid systems. It is found that the low frequency scattering can be described by correlated configurations that include more than one mobile ion. Specifically it is shown that the interactions of the mobile ions can lead to distortions that can account for the depolarized character of the low frequency scattering. Specific configurations of the mobile ions are discussed, and the width of the narrow spectral component can be related to the diffusion constant and the ionic conductivity.

HIGH PRESSURE STUDIES OF FAST ION CONDUCTORS OF THE MERCURY AND SILVER IODIDE TYPE*

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High pressure effects on the Raman spectra of Ag_2HgI_4 and Cu_2HgI_4 will be reported and compared with high temperature studies. Temperature and pressure effects will be related to the observed phase changes, and to the changes in electrical conductivity. The response of the low-frequency vibrations to high pressure indicate the importance of pressure measurements as a probe in determining anharmonicity in fast ion conductors.

Preliminary investigations on new fast ion conductors of the pyridinium pentasilver-hexaiodide type will be presented. Effects of pyridine ring substituents on the conductivity will be cited. Possible synthetic directions to obtain new improved fast ion conductors of this type will be discussed.

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*Work performed under the auspices of the Office of Basic Energy Sciences of the U. S. Department of Energy.

DYNAMICAL AND CRITICAL POINT PROPERTIES OF $RbAg_4I_5$*

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The results of a comprehensive study of the critical point properties of $RbAg_4I_5$ near the 208K phase transition will be presented. Specific heat data, ionic conductivity, and birefringence measurements have been combined to produce a complete set of exponents: $\alpha = 0.14 \pm 0.02$, $\beta = 0.35 \pm 0.02$, and $\gamma = 1.25 \pm 0.1$. These satisfy the scaling law $\alpha + 2\beta + \gamma = 2$, within experimental error. The last of these exponents was obtained by a new method involving the critical depolarization of light by fluctuations in the isotropy of the index of refraction. The Ising-like nature of these exponents, and the linear coupling between strain and the order parameter, has led us to propose a Jahn-Teller-like model for the transition, involving the coupling of site occupancies through lattice distortions. The ionic conductivity in the critical region has been demonstrated to be closely related to the specific heat in $RbAg_4I_5$ and its K and NH_4 isotypes. This demonstrates the importance of short-range correlations in determining the ionic conductivity. A detailed neutron scattering study has revealed the presence of a pervasive, low energy excitation mode in both superionic phases. The mode is propagating at 125K with an energy of 2 meV, and very little dispersion. It appears at all positions in the zone with nearly equal intensity. At higher temperatures, the mode broadens gradually. Acoustic phonons can be observed at low k-values; however, these disappear as their energies approach the 2 meV band. Above 2 meV, no phonon modes were observed despite the fact that over 100 optical modes should be present. These results are taken as further evidence of strong coupling between lattice modes and mobile ions.

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DIFFUSION AND CONDUCTIVITY IN SUPERIONIC CONDUCTORS

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This paper concerns the effects of disorder on mobility and structure in solid electrolytes and other dense inhomogeneous systems. An important quantity is the range, 2V, through which interactions among the mobile particles spread the one particle energies about their average value. Depending on the size of V/K_BT, the assembly exhibits the structural properties of glass-like behavior, order-disorder transformations as in hydrides and $RbAg_4I_5$, liquid-like blocked mobility (AgI), thermally activated defect structure, etc.

In a general treatment of the diffusion dynamics, using classical statistical mechanics, it is found that a second parameter of this type also plays a central role in the mobility process. It measures the spread of saddlepoint potentials caused by interactions among the mobile particles. For this reason, blocking models of the diffusion, which neglect the effect of disorder on the dynamics, omit one of the main mechanisms by which disorder modifies the mobility. An accurate connection between thermal and diffusion proprerties in $RbAg_4I_5$ is obtained from the present theory.

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EFFECT OF ADDITIVES AND MOISTURE ON THE IONIC CONDUCTIVITY OF Li_5MO_4 (M = Al, Ga, Fe)**

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The ionic conductivity of polycrystalline Li_5MO_4 (M = Al, Ga, Fe) materials can be significantly affected by the environment as well as by additives. Effects associated with Li_2SO_4 additions, moisture and the carrier gas (air, O_2, and Ar) have been examined. The intrinsic materials in the dry state have similar conductivity characteristics. The conductivity is thermally activated (activation energies of ∿0.5 to 1.0 eV) with values ranging from 10^{-4} to 10^{-3} $(\Omega\text{-cm})^{-1}$ at 500°C. The lack of O_2 in the environment appears to increase the activation energy, suggesting that the O_2 partial pressure may affect the defect and/or impurity characteristics. LiOH is formed within the material (surface and grain boundary regions) upon exposure to moisture, and produces a dramatic increase in the conductivity by several orders of magnitude above ∿400°C. The conductivity at 500°C depends upon the water vapor pressure and can be reproducibly altered by cycling between wet (containing LiOH) and dry (no LiOH) states. The addition of Li_2SO_4 to Li_5AlO_4 increases the total conductivity in the dry state (by a factor of 10-100), while decreasing the electronic contribution to the conductivity. Upon exposure to moisture the transaction to the high conductivity state is shifted to a lower temperature (∿350°C) due to formation of a Li_2SO_4-LiOH eutectic. The Li_5AlO_4 + Li_2SO_4 materials in the dry state are stable in liquid lithium. This combined with their ionic conductivity at high temperature [$\sim 10^{-1}(\Omega\text{-cm})^{-1}$ at 600°C] may make them useful as solid electrolytes for high temperature batteries.

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VITREOUS SOLID ELECTROLYTES*

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A new class of glasses, which have high ionic conductance (~ 1 S m^{-1} at 25 ^{o}C), have been prepared by quenching melts composed of mixtures of silver iodide and a silver oxosalt. Such materials may occupy an interesting position between crystalline solid electrolytes and molten salts. In addition, useful comparisons can be made between their electrical properties and those of more conventional glasses.

In spite of the thermodynamic instability of vitreous phases, many of these glasses are stable in practice, over extended periods in ambient conditions. This property, together with the advantages of their glassy nature (e.g. their ability to be formed into films by splat techniques) makes them suitable for consideration for practical applications.

In this paper attention is focussed principally on glasses originally obtained and characterised in our laboratories. These include materials prepared from mixtures of AgI and Ag_3AsO_4, $Ag_2Cr_2O_7$ or $Ag_2Mo_2O_7$. After a brief review of their physico-chemical properties, features of the conduction mechanism are discussed and some comparisons are made with the electrical behaviour of other glasses. Finally electrochemical studies of a number of cells are described.

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ELECTROCHEMICAL PROPERTIES OF SOME SOLID LITHIUM ELECTROLYTES

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In this paper some of our studies on solid lithium electrolytes are reviewed. The emphasis has been toward studying solid lithium systems which could be used in power sources. The lithium ion conductors of interest are presented covering three main topics:

i) the crystallographic structure including the possible defect mechanism responsible for the ionic conduction
ii) the temperature dependence of the ionic conductivity for the determination of the ion conduction and
iii) the chemical and electrochemical stability of the system at high lithium activities to check the potential application with lithium electrodes.

The solid lithium ion conductors of current interest are discussed with reference to their crystal structure. Thus the LiI system representative of the rock salt structure will be compared with $Li_9N_2Cl_3$, with the antifluorite structure, $Li_{14}Zn(GeO_4)_4$, representing the "Lisicon" structures and Na-Li-ß-alumina and Li_3N, materials having layered structures. Finally the potential application of these electrolytes in power sources will be discussed.

STRUCTURE AND ION TRANSPORT IN β'' ALUMINA

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Research has been undertaken at the Laboratoire de Cristallographie (C.N.R.S.) and at the Institut-Laue-Langevin to determine the structural basis for superionic conductivity in the rhombohedral β''-alumina structure. Quasi-elastic neutron scattering and D_2O-H_2O exchange have been used to study proton diffusion and bonding in H_3O^+-β'' alumina. The local arrangements of the conduction ions in Na^+-β'' alumina and H_3O^+-β'' alumina are being investigated by X-ray and neutron diffraction and diffuse X-ray scattering at low temperature.

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CHEMISTRY AND CONDUCTIVITY OF PROTONIC BETA ALUMINAS

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We have measured the thermal stability (25-900°C) and ionic conductivity (25-250°C) of single crystals of NH_4^+ beta alumina ($1.15(NH_4)_2O \cdot 11Al_2O_3$) and $NH_4^+/H(H_2O)_x^+$ beta" alumina ($((0.83-y)NH_4+yH(H_2O)_x)_2O \cdot 0.33MgO \cdot 5Al_2O_3$). The samples were prepared by ion exchange of the sodium isomorphs in ammonium nitrate at 200°C. Sodium beta alumina was obtained from the Union Carbide Corporation and sodium beta" alumina crystals (typically 6mm x 4mm x 2mm) were grown at 1700°C from a melt containing Na_2O, MgO, and Al_2O_3.

Ion exchange of sodium beta alumina crystals (10mm x 3mm x 0.5mm) results in complete replacement of the sodium ions by ammonium ions in about 14 days. Similar sodium beta" alumina crystals exchange in 8-10 days but form a composition in which only 50-80% of the substituting ions are NH_4^+. The balance is presumably $H(H_2O)_x^+$.

NH_4^+ beta alumina loses NH_3 between 350-425°C to form H^+ beta alumina. It completely decomposes above 750°C. $NH_4^+/H(H_2O)_x^+$ beta" alumina loses NH_3 and H_2O from 225-350°C. It undergoes partial, irreversible decomposition at 450-500°C followed by complete decomposition above 750°C.

Conductivity was measured using two probe, complex ac analysis. NH_4^+ beta alumina yielded poorly resolved complex admittance plots. An estimate of its conductivity is 10^{-3} (ohm cm)$^{-1}$ at 250°C. $NH_4^+/H(H_2O)_x^+$ beta" alumina produced good admittance plots. Its conductivity varies with composition but is about 1×10^{-4} (ohm cm)$^{-1}$ at 25°C. The charge carrying species in each compound is not known.

Wide line NMR measurements on single crystals have provided insight into the nature of ionic motion and bonding in each composition.

Thermodynamic and Transport Properties of Selected Solid Solution Electrodes

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To facilitate the design and optimisation of batteries incorporating solid solution electrodes it is desirable to know how the following properties of the mobile species (j) very with composition and temperature, $\Delta\bar{G}_j$, $\Delta\bar{H}_j$, $\Delta\bar{S}_j$, σe, σi, $\tilde{D}_j$, D^*_j, ΔE_j. We have already reported (1,2) how these data may be conveniently measured using an automated solid state eight point conductivity and titration apparatus. More recent measurements on $Cu_xMo_6S_{8-g}$, $Li_xMo_6S_{8-g}$, and Li_xTiS_2, will be discussed with particular relevance to simple statistical models used to predict the variation of the partial thermodynamic quantities with composition. In the case of the Chevrel phase, $Cu_xMo_6S_{8-g}$ these models have also been used to interpret the ionic conductivity behaviour in terms of the distribution of copper ions over the available sites.

The preceding data has also been used to predict overpotential behaviour in solid state cells so that typical 1-V characteristics can be calculated and compared to experimental values.

(1) G.J. Dudley and B.C.H. Steele, J. Solid State Chem, 21, 1, 1977

(2) G.J. Dudley and B.C.H. Steele, J. Electrochem. Soc. 125, 1994, 1978.

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ABSTRACTS

of

CONTRIBUTED PAPERS

Poster Session PA

FABRICATION OF β''-Al_2O_3 TUBES FROM CAST CERAMIC TAPE*

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Most conceptions of the sodium/sulfur batteries that may eventually see commercial use in electric vehicles or stationary energy storage applications show in each cell a tube-shaped sodium ion-conducting ceramic electrolyte. Presently such tubes are fabricated by one of several batch ceramic processes based on electrophoresis and isostatic pressing. These methods of production cause the electrolyte component to be inherently costly. These processes are additionally limited in their ability to produce thin-walled tubes, which limitation is reflected in higher internal resistance and reduced performance of the battery.

A novel alternative approach is here proposed for fabricating thin wall ($\sim$0.3 mm) β''-Al_2O_3 tubes from cast ceramic tape. The fabrication process and characteristics of the fired tubes are described.

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PA-2

PROCESSING AND PROPERTIES OF SODIUM β''-ALUMINA AND NASICON CERAMIC ELECTROLYTES

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and

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The sodium superionic conductors sodium β''-alumina and NASICON (of formula $Na_3Zr_2PSi_2O_{12}$) have been processed as polycrystalline forms under varying processing conditions. Several properties have been measured and include mass density, sodium ion electrical resistivity, thermal expansion coefficient, fracture strength, microstructural character, long and short term stability to liquid sodium and water.

Advantages and disadvantages of several processing methods and an initial comparison of the chemical and physical characteristics of the sodium β''-alumina and NASICON are made. Special emphasis is directed toward chemical and electrolytic stability in some chemical environments.

*Supported by the U.S. Department of Energy

PA-3

DEGRADATION OF RAPID ION CONDUCTORS UNDER ELECTROLYTIC CONDITIONS

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Strength degradation of sodium β"-alumina is examined as a function of grain size and temperature. Sodium - β" - sodium cells have been constructed and operated at current densities up to 4.5 amps/cm^2 without immediate failure. Critical current densities over which degradation occurs are examined in light of the theoretical model presented previously. The role of impurities as well as wetting characteristics of β"-alumina by sodium are discussed in light of the proposed model. Implications regarding cell design are presented. Finally, recommendations are made with regards to the use of other rapid ion conducters in similar systems.

*Supported by the Department of Energy

PA-4

THE HEAT TREATMENT OF BETA-ALUMINA

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At a relatively early stage in the developing of sintering process for β-Al_2O_3 tubes it was found that post-sintering heat treatment at a temperature lower than the sintering temperature gave an increase in ionic conductivity. This was achieved without any reduction in strength and resulted in improved performance in sodium-sulphur cells.

The present work is concerned with a detailed study of the effects of heat treatment on three β-Al_2O_3 compositions. The improvement in ionic conductivity was correlated with an increase in volume fraction of the more conductive β'' phase and changes in the microstructure. The heat treatment temperature/time is limited by the onset of discontinuous grain growth which weakens the ceramic. There were significant differences in the grain size distributions of heat treated samples depending upon ceramic composition. The ionic conductivity of material with a lower soda and dopant level is less affected by heat treatment and this composition also proved to be less susceptible to secondary grain growth. The secondary grains in this material were acicular, whereas in the materials with higher soda and dopant levels the grains tended to be more equiaxed. The reasons for these differences in behaviour are discussed and the ways in which heat treatment can be used to improve the properties of beta-alumina in sodium-sulphur batteries are considered.

SHORT PERIOD β-ALUMINA TYPE COMPOUNDS*

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Microsyntactic Intergrowth observed in Mg-doped β-alumina indicates a possible existence of a series of β-alumina type compounds of various periods[1] [with inter-conduction layer distance of 6.5A°, 11A° (β-alumina) 15.5A° (β'''-alumina), 20A°, etc.]. Crystal chemical concept of microsyntactic intergrowth of β-alumina type compounds has since been confirmed,[2] although compounds with inter-conduction layer distance other than that of 11A° and 15.5A° do not seem to exist in equilibrium in the composition range of the specimens used. Since, in such compounds, the ionic conductivity should be proporational to the density of conduction layers, we tried to synthesize short period compounds (6.5A° inter-conduction layer distance) in an effort of searching for new materials with superior conductivity. Such compounds are located at the composition around $Na_{0.9}\ Ti_{1.1}\ Fe\ O_4$, and one of these has been identified. This has an orthorhombic symmetry and deviates somewhat from β-alumina structure, but has fundamental characteristics of short period β-alumina. This compound is found to be a "superionic" conductor and the activation energy of ionic conduction is around 0.1 eV.

*Supported in part by NSF DMR 7502959

**Present address: Tokyo Institute of Technology, Oh-okayama, Tokyo, Japan

[1] H. Sato and Y. Hirotsu, Mat. Res. Bull. 11 1307 (1976)

[2] H. Sato, Y. Hirotsu and H. Kuwamoto, Proc. Modulated Structures Seminar, 1979

PA-6

SODIUM β"-ALUMINA AT HIGH CURRENT DENSITY

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Ceramic β"-alumina electrolytes operated in Na-S or Na-Na cells exhibit an apparent critical current density in the range of 0.5 to 1 A/cm^2 above which rapid degradation and failure of the electrolyte occurs. Considerable work has been directed toward understanding this phenomenon which limits the useful rates at which Na-S battery cells can be recharged. In the course of our experiments on Sodium Heat Engine systems, at 700-1000° C, we routinely draw sodium ion currents of 1-2 A/cm^2 to sample electrodes on β"-alumina. We have conducted specific tests in which ionic current densities up to 15 A/cm^2 were passed by β"-alumina of 1 mm wall thickness with no apparent change in the current-voltage relation. In contrast to the usual situation in Na-Na cells or in the recharging of Na-S cells, the Sodium Heat Engine conditions never involve the presence of a liquid sodium phase at the exit surface of the ceramic.

Our results demonstrate that for ionic current densities an order of magnitude greater than the "critical", no intrinsic instability of β"-alumina occurs. These results are consistent with the degradation mechanisms previously proposed by Richman and Tennenhouse.[1]

[1] R. H. Richman and G. J. Tennenhouse, J. Am. Ceram. Soc. 58, 63 (1975).

ELECTRICAL RESISTIVITY OF BETA-ALUMINA SOLID ELECTROLYTES FROM 200 TO 1000 C

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The resistivities of dense polycrystalline samples of β-alumina, β"-alumina and mixed β, β"-alumina have been measured by DC techniques over the temperature range of 200 to 1000 C. Porous molybdenum contacts in a sodium vapor atmosphere served as reversible electrodes. The resistivity of commercial lithia stabilized β"-alumina was found to obey the empirical relation $\rho = T[\ a \exp(b/T) + c \exp(d/T)]$, with $a = 5.05 \times 10^{-4}$ ohm cm K^{-1}, $c = 1.75 \times 10^{-7}$ ohm cm K^{-1}, $b = 1430$ K and $c = 4965$ K. At high temperatures the apparent activation energy is 2.84 Kcal while at low temperatures the apparent activation energy is 9.87 Kcal.

PA-8

ALL SOLID STATE ELECTROCHROMIC CELL BASED ON ANODIC IRIDIUM OXIDE FILMS (AIROFs)

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We report on the fabrication and electrochromic properties of a new all solid-state electrochromic cell based on AIROFs. The cell consists of a symmetric cell AIROF/solid electrolyte/AIROF. Preliminary devices show good contrast with response times < 0.5 sec. for driving voltages < 1V. Other cells using the AIROF/solid electrolyte half cell, but with other mixed conductors as counter electrode, also will be discussed.

IONIC CONDUCTION IN ELECTROCHROMIC ANODIC IRIDIUM OXIDE FILMS

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Display devices based on solid electrochromic materials derive their operation from a reversible color change caused by a change of valence in the material due to electron transport, accompanied by ionic transport within the solid to maintain overall charge balance. For example, it is generally accepted that electrocoloration of WO_3 films occurs by simultaneous injection of electrons from the back electrode and protons or other small cations from the electrolyte solution.

A new electrochromic material, the anodic iridium oxide film or AIROF, has been found to color and bleach in aqueous solutions considerably faster than WO_3 films.[1] A proton-electron injection mechanism has also been proposed to account for AIROF electrochromism.[1] However, tests of AIROF electrode performance in nonaqueous acid electrolytes show that no color change can be induced in these media despite the presence of ample free protons, casting doubt on a proton mechanism. Recent experimental results bearing on the nature of ionic conduction and electrochromism in the AIROF will be discussed.

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[1] S. Gottesfeld, J. D. E. McIntyre, G. Beni and J. L. Shay, Appl. Phys. Lett. 33, 208 (1978).

PA-10

RECENT STUDIES OF SULFATE-BASED SOLID ELECTROLYTES

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Between 575° and 860°C Li_2SO_4 has a fcc phase, which according to our neutron and X-ray diffraction studies is a rotator phase. From space considerations it follows that the rotation of the sulfate ions is strongly coupled, and that the size of the cation positions is not constant. This rotation of the sulfate ions explains why all mono- and divalent cations are mobile in sulfate-based solid electrolytes.

The latent heat of the phase transition is 23 kJ/mol for pure fcc Li_2SO_4, and it is of the same order for binary and ternary mixtures with other sulfates. Thus, sulfate mixtures might be used for storage of thermal energy in the range 100 - 800°C.

Plastic deformation of fcc Li_2SO_4 has been studied above 781°C. Thixotropic behaviour was observed with a relaxation time of 8.4 h at 781°C.

The refractive index of Li_2SO_4 has been determined very accurately over a temperature range including the fcc phase as well as the melt.

A number of cells with sulfate-based electrolytes have been tested.

LOW TEMPERATURE DEGRADATION IN THE SOLID STATE BATTERY $Ag/RbAg_4I_5/I_2$

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Solid state cells of the type $Ag/RbAg_4I_5/QI_5$ or QI_9, where Q^+ represents the tetramethylammonium ion, were stored for five years at 71°C, 23°C and -15°C. The set stored at -15°C showed significant increases in resistance when the $RbAg_4I_5$ electrolyte was formulated with small amounts of both powdered silver and Rb_2AgI_3 (Set A); this suggests that some of the $RbAg_4I_5$ disproportionated into the more resistive AgI and Rb_2AgI_3 phases. In contrast cells which lacked Rb_2AgI_3 in the electrolyte (Set B) did not increase in resistance. Apparently the presence of both product phases in the electrolyte of Set A is important in nucleating the thermodynamically favored low temperature decomposition of $RbAg_4I_5$.

Microcalorimetric measurements at 37°C were made on cells from Set A. Those stored at temperatures of 71° or 23° exhibited exothermic outputs of 0.2 to 0.5 μwatt, whereas batteries stored at -15°C had endothermic outputs of -6 μwatt, consistent with reversal of the decomposition reaction.

PA-12

DECOMPOSITION OF NITRIC OXIDE USING SOLID STATE ELECTROLYTE

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Decomposition of NO has been studied on an electrochemically reduced surface of scandia-doped zirconia. Experiments conducted at 900°C with mixtures of 2.9 m/o and 5.1 m/o NO in He showed that extremely high decomposition rates can be obtained for NO upon zirconia under sufficiently reducing conditions. These rates are more than 6 orders of magnitude larger than those found for zirconia under normal conditions, and 3 orders of magnitude greater than those for supported Pt catalysts. This unusually high reaction rate is evidently due to the presence of a very high concentration of both electrons and oxygen vacancies in the surface region of the electrochemically reduced zirconia. A simple electrochemical cell which eliminates the need for large electrode areas and leak-tight two-compartment geometries which can be used for such purposes has been demonstrated.

PA-13

SOLID ELECTROLYTE/POROUS ELECTRODE KINETICS

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As an example of a solid electrolyte/porous electrode system, carefully prepared porous Pt/8 m/o $Sc_2O_3.ZrO_2$ interfaces have been studied by both AC admittance and 4-probe DC polarization techniques between 600° and 900°C. The electrical response of the interface between 40 Hz and 20 kHz in air ambient was analyzed by use of complex plane techniques. An equivalent circuit composed of a pure interface resistance in parallel arrangement with an interface impedance $Z_i^* = A_1\omega^{-\alpha} - jA_2\omega^{-\alpha}$ fit the experimental data well. The impedance parameters A_1 and A_2 exhibited an activation enthalpy half of that for ionic conduction.

Steady-state DC polarization studies carried out in an oxygen partial pressure range of 1 to 10^{-6} atm showed two current plateaus. Limiting currents at high ionic fluxes were due to slow diffusion of molecular oxygen in the gas phase. Porous Pt electrodes were practically nonblocking at intermediate fluxes and sufficiently high oxygen pressures due to fast interface kinetics. A thermally activated diffusional process, independent of oxygen partial pressure, was found important at low overvoltages, and was attributed to slow diffusion of electrons from the Pt electrode to the electrochemical reaction site. The disappearance of these low overvoltage current plateaus above 700°C was correlated with the transformation of the Pt surface structure from a "reconstructed" to a "restored" state.

PA-14

THERMODYNAMIC PROPERTIES OF THE SOLID ELECTROLYTE $LiAlCl_4$

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Lithium aluminum chloride ($LiAlCl_4$) has shown fast transport of lithium ions in both solid and molten states (mp. 146 C), with a negligible electronic contribution (1). Preparation and handling are simple, making this material a potential candidate for technological applications in galvanic cells.

To select proper electrode materials one needs to know the thermodynamic range of lithium activity compatible with the electrolyte. Solid state electrochemical measurements have been used to obtain this information for $LiAlCl_4$. It was employed as an electrolyte in the cell

$$Al,LiAl\ /\ LiAlCl_4/\ Al,AlCl_3$$

and as an electrode in a second type of experiment using cells of the type

$$Al,LiAl\ /\ Li_4SiO_4 - 40\ m/o\ Li_3PO_4\ /\ Li_{1+x}AlCl_4$$

in which the lithium content was varied over the range of existence.

This compound is thermodynamically stable at lithium activities between $10^{-28.4}$ and $10^{-73.7}$ at 25°C. The phase width is as small as 10^{-4} m/o. The standard Gibbs free energy of formation of $LiAlCl_4$ is -1.051 MJ/mole at 25°C. The effective electronic mass, the band gap, and the intrinsic disorder may also be estimated from the results.

It is concluded that the range of lithium activity over which $LiAlCl_4$ is stable precludes its use in rechargeable cells with elemental lithium electrodes. It might be used in cells involving electrodes operating at sufficiently low lithium activities, or in other applications, such as electrochromic displays or memory elements.

(1) W. Weppner and R. A. Huggins, J. Electrochem. Soc., 124, 35 (1977).

USE OF SOLID OXIDE ELECTROLYTES FOR THE STUDY OF OXYGEN SOLUBILITY AND DIFFUSIVITY IN LIQUID METALS*

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Solid electrolytes have been applied extensively for the study of the thermodynamics of solid and liquid systems and for the transport of specific species using several electrochemical techniques -- potentiostatic current measurements and coulometric-potentiometric titrations -- for determining some fundamental properties of liquid metal-oxygen systems, particularly for systems with limited oxygen solubility and relatively low saturation oxygen activity. The properties of interest include: The diffusion coefficient of oxygen, D(O), in pure liquid metals and in liquid metals alloys; the thermodynamic activity of oxygen as a function of oxygen composition; the solubility and maximum solubility of oxygen in liquid metals; the Gibbs free energy of formation of respective oxides; the thermodynamics of binary liquid metals solutions; and solute interactions in liquid metal solutions. Typical liquid metals include Ga, In, Sb and Bi. A brief survey of typical results will be given. Major emphasis, however, will be devoted to a discussion of experimental problems and sources of error that arise from the electrolyte and electrode degradation.

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PA #37

PA-16

NEW TYPE OF CAPACITORS

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On the basis of the investigations made a new type of capacitor with a larger capacitance and using a solid electrolyte has been designed. One of the capacitor electrodes is able to accumulate charges in the bulk, which enables to obtain specific capacitance reaching 80F/cm^3 (at 25°C). Great characteristic parameters of the device make the possibilities of miniaturization much wider.

The capacitor shows the stability of capacitance values within a wide temperature range (0 - +85°C). Electronic resistance of the system reaches 10^9 ohms, so the charge retains for a long period of time.

Capacitors CBC may be charged by pulse currents as well, the capacitance value being not dependent on the pulse frequency of the current supplied.

This type of capacitors may find a wide application in various radio-electronic devices.

ABOUT SOME STUDIES ON ACCELERATED ELECTROFORMING OF PLUMB ACCUMULATOR PLATES

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The use of current with different waveform in electroforming of plumb accumulator active mass, leads to a considerable change of the electrochemical system parameters. Via the recurrent alteration of current polarity, the active internal resistance of the system varies considerably which accelerates the ion transfer in the electrolyte and the forming mass, and correspondingly the electrochemical process for obtaining spongy plumb and plumb dioxide on the electrodes is intensified many times.

The scientific results as obtained are highly valuable for the practice and find application in the production of plumb accumulators and armoured batteries in our country.

PA-18

CHEMICAL DIFFUSIVITY OF LITHIUM IN Li_xTaS_2 AND Li_xTiS_2 AT 30°C*

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The layered group IV and V transition metal dichalcogenides have received considerable attention as potential cathodes in secondary lithium batteries. The practical application of these materials strongly depends on the diffusivity of lithium in the two dimensional van der Waals gap; the magnitude of the lithium diffusivity controls the current density in the cathode.

The chemical diffusivity of lithium in Li_xTaS_2 and Li_xTiS_2 $(0 < x < 1)$ was determined at 30°C by a current-pulse relaxation technique in an electrochemical cell:

$$Li/Li^+ \text{ } (LiC\ell O_4 \text{ in propylene carbonate})/Li_xMS_2 (M = Ta \text{ \& } Ti).. \qquad (A)$$

These measurements were made using polycrystalline electrodes in which chemically prepared intercalated disulfides (-325 mesh) were isostatically pressed to form cathodes of ∿7 mm dia. lithium was injected into or removed from the cathode by constant current-pulses (∿1 mA) for short times (3-13 secs). The chemical diffusivity of lithium was calculated from the decay rate of the transient voltage. The chemical diffusivity of lithium in Li_xTiS_2 is 5×10^{-9} cm^2/sec over the entire composition range. The chemical diffusivity of lithium in Li_xTaS_2 is composition dependent, and the average value is 1.8×10^{-8} cm^2/sec in the composition range of $0.25 < x < 0.75$ at 30°C.

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SYNTHESIS, CHARACTERIZATION AND UTILIZATION OF $M_5ErSi_4O_{12}$ COMPOUNDS AS SOLID ELECTROLYTES IN ALKALI METAL-TiS_2 CELLS*

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High sodium ion conductivity has been reported for trivalent metal silicates such as $Na_5GdSi_4O_{12}$ (1) and $Na_5YSi_4O_{12}$ (2). Forty seven percent of the sodium ions in the latter are shown to be mobile in its framework structure which permits three dimensional conductivity. Although other sodium lanthanide silicates are suggested to be similar (1) no detailed conductivity studies are presently available.

We have synthesized the erbium analog and employed in the high temperature sceondary cell $Na/Na_5ErSi_4O_{12}/TiS_2$. The electrochemical behavior of this cell is reported as a function of temperature, time, and charging voltage at various resistive loads. Because of the ease of Li intercalation in TiS_2 this research has also been directed towards the development of a solid lithium ion conductor by successive replacement of the sodium in the compound with lithium for use in the corresponding Li/TiS_2 cell. The synthesis of two of these compounds, $Li_2Na_3ErSi_4O_{12}$ and $Li_5ErSi_4O_{12}$, has been accomplished. X-ray diffraction data of these compounds indicate that they have similar, but individually unique structures.

*Supported by the U.S. Air Force Aero Propulsion Laboratory

1. R. D. Shannon, H. Y. Chen, and T. Berzins, Mat. Res. Bull. 12, 969(1977).

2. H. Y-P. Hong, J. A. Kafalas, and M. Bayard, Mat. Res. Bull. 13, 757(1978).

PA-20

RECENT INVESTIGATIONS OF SOME ION-CONDUCTING OXIDES

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The application of solid electrolytes in energy-conversion and energy-storage systems is described. Some fundamental aspects of fast ion conductors are summarized. The principles are illustrated with recent research results using δ-Bi_2O_3, $Ag_xV_2O_5$ and La-Co based perovskites as solid electrolytes.

Structural and thermodynamic data of Bi_2O_3 will be presented. Present research is directed to improving the stability of the material against reducing atmospheres and to enlarging the stability range of the good ion-conducting δ-phase to lower temperatures.

$Ag_xV_2O_5$ is a mixed conductor with remarkable thermodynamic properties, showing an increased stability (versus Ag and V_2O_5) at higher temperatures. The low Ag^+-mobility prevents its use as a solid electrode material.

Investigations of La-Co based perovskites has led to an electrochemical method to determine very small diffusion coefficients of oxygen ion vacancies in electronically conducting oxides. Favorable oxygen evolution characteristics have been observed for several of these perovskites when used as electrode material in the electrolysis of water.

ANALYSIS OF THE ALTERNATING CURRENT PROPERTIES OF LISICON CERAMICS*

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The ionic conductivity of polycrystalline ceramic pellets of LISICON ($Li_{14}Zn(GeO_4)_4$) has been determined over the temperature range from 298 to 573 K by complex impedance measurements at frequencies from 5 Hz to 108 MHz. For temperatures up to 480 K the grain and intergrain contributions to the ceramic conductivity have been separated and their activation energies (0.89 and 0.76 eV, respectively) have been determined. The measured ceramic conductivity decreases markedly with increasing time of exposure to air at room temperature. This change can be attributed to the moisture sensitivity of the intergrain regions, since the grain contribution to the conductivity does not vary significantly with exposure time. The highest measured ceramic conductivity at $300^{\circ}C$, which was determined immediately after sintering, is $0.1\ \Omega^{-1}\ cm^{-1}$, in good agreement with the value reported by Hong[1] and nearly an order of magnitude higher than that reported by von Alpen *et al.*[2]

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*This work was sponsored by the Department of Energy.

†Present address: GTE Laboratories, Waltham, MA 02154.

[1] H. Y-P. Hong, Mater. Res. Bull. 13, 117 (1978).

[2] U. v. Alpen, M. F. Bell, W. Wichelhaus, K. Y. Cheung, and G. J. Dudley, to be published.

PA-22

COMPOSITIONAL DEPENDENCE OF THE IONIC CONDUCTIVITY IN THE PYROCHLORE TYPE SYSTEMS $Me_{1+x}Ta_{1+x}W_{1-x}O_6$, Me=Na, K, Tl.

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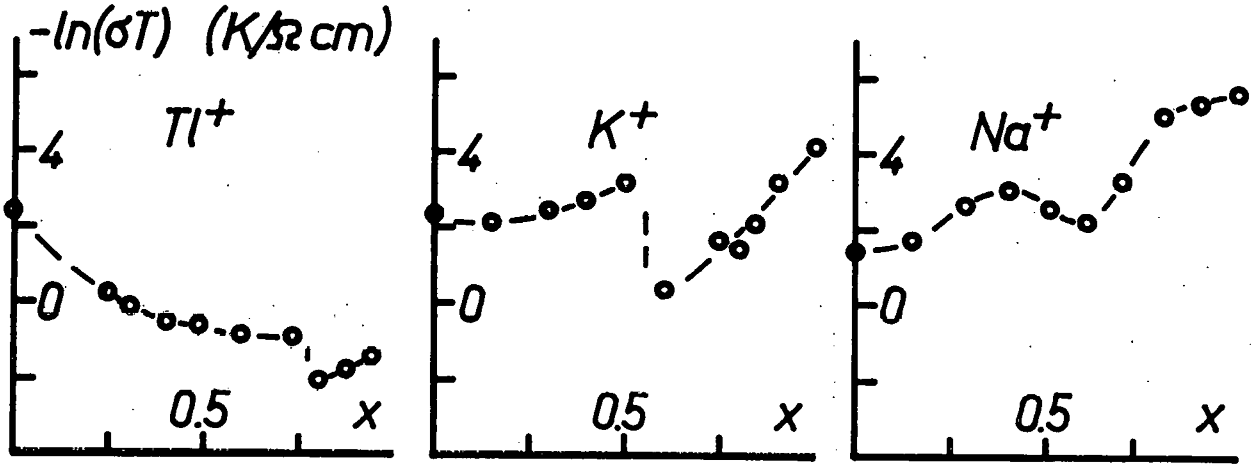
The ionic conductivity of the pyrochlore type system $Me_{1+x}Ta_{1+x}W_{1-x}O_6$ ($0 \leq x \leq 1$, Me=Na, K and Tl) has been determined at elevated temperatures by means of computer controlled impedance measurements. The compositional dependence of the ionic conductivity at 675 K is given below. Values for activation energy and the preexponential factor in the Arrhenius equation for the three systems will be presented. It has been possible[1] to relate the $\ln(\sigma T)$ values for $0 < x < 1$ in the Tl system to the occupancy factors for the Tl^+ ions at the crystallographic sites (16d) and (8b). Corresponding correlation for the Na and K systems will be discussed.



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[1] J.Grins, M.Nygren and T.Wallin, submitted for publication.

PA-23

CRYSTAL STRUCTURE AND IONIC CONDUCTIVTY OF A NEW SUPERIONIC CONDUCTOR, $Na_3Sc_2P_3O_{12}$*

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A new solid electrolyte, $Na_3Sc_2P_3O_{12}$, a structural analog of NASICON ($Na_3Zr_2Si_2PO_{12}$), has been synthesized by solid state reaction and by a flux method. The ionic resistivity of a cold-pressed and sintered pellet with only 75% of theoretical density was determined to be 12 Ωcm at 300°C, with an activation energy of 0.25 eV.

While single crystals of NASICON have never been obtained, single crystals of $Na_3Sc_2P_3O_{12}$ were grown from an excess of $Na_4P_2O_7$ as a flux. A cube-shaped crystal was selected for single-crystal x-ray diffraction analysis. The structure is monoclinic with space group C2/c and cell parameters a = 15.461, b = 8.913, c = 9.016 Å and β = 124.80°. The basic structural feature is a rigid three-dimensional network formed by ScO_6 octahedra and PO_4 tetrahedra. Each octahedron is connected to six tetrahedra, while each tetrahedron is connected to four octahedra. The Na^+ ions are randomly distributed at three different sites. The temperature coefficients of those positions are abnormally high, consistent with the high mobility of the Na^+ ions.

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PA-24

STRUCTURAL RELATIONSHIPS IN SOME SULPHATES AND ORTHOPHOSPHATES

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Almost all oxy-acid salts with tetrahedral anions have well-ordered structures at low temperatures, but several transform to high-temperature modifications in which the anions are highly disordered. Appreciable cationic mobility is observed in some of these phases, eg. Na_3PO_4, Ag_3PO_4, Ag_2SO_4. We have examined several systems using single crystal x-ray and powder neutron diffraction (PND) techniques.

Ag_3PO_4 ($P\bar{4}3n$, a=6.0095(6)Å, Z=2) has well ordered PO_4^{3-} groups at room temperature but slightly disordered Ag. Na_3PO_4 is tetragonal at room temperature, $P\bar{4}2_1m$, a=10.774Å, c=6.816Å, Z=8. Both transform to cubic FCC phases at high temperature with highly disordered PO_4^{3-}. In γ-Na_3PO_4 two sodium sites are distinguished, but in the solid solution $Na_{3(1-x)}Al_x\square_{2x}PO_4$, where the cubic phase is stabilised to lower temperatures, for x=0.2 vacancies are present on only one sodium site.

Like Ag_3PO_4, monoclinic Ag_2SO_4 (C2/c, a=5.818(2)Å, b=12.702(3) Å, c= 5.893(1) Å, β=119.55(1)°, Z=4) has slightly unusual Ag positions at room temperature. The high temperature phase is hexagonal, $P6_3/mmc$, similar to that of β-K_2SO_4. PND results for these two systems are compared.

STRUCTURE ANALYSIS OF $Na_4Zr_2Si_3O_{12}$ AT 300°C AND 600°C IN RELATION WITH THE IONIC CONDUCTIVITY.

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Compounds of the series $Na_{4-x}Zr_2Si_{3-x}P_xO_{12}$ are well known good ionic conductors for $0.1<x<1$ while the end member $Na_4Zr_2Si_3O_{12}$ is only a rather moderately good conductor. Yet, because single crystals of the end member were easily grown by hydrothermal synthesis, we decided to investigate his structure at 300°C and 600°C in order to determine the structural aspects which can explain the large increase of the conductivity of this material versus the temperature. Intensity data for a spherical crystal of $Na_4Zr_2Si_3O_{12}$ were collected on a Philips four-circle diffractometer using AgK_α radiation. The crystal was heated using a hot air device designed by Capponi and Argoud. Both 300°C and 600°C structure refinements were carried out in space group $R\bar{3}C$. In order to study the distribution of Na(1) and Na(2) about their respective sites, Fourier maps were calculated at room temperature and 300°C. At 300°C, no significant deformation of Na(1) electron density was observed nor were any residual peaks observed in the regions between Na(1) and Na(2) sites. However an unusual deformation of the Na(2) electron density was observed and well definite peaks between Na(2) sites could be seen which did not exist at room temperature. As the major thermal ellipsoid of Na(2)turns toward the Na(2)-Na(2)direction,and as the minimum opening radia between these two sites increases from 1.15 to 1.22 Å, one must consider that pathway as more and more favorable for the displacement of Na^+ cations ($RNa^I = 1,15$ Å) when the temperature increases. The results obtained from the data collected at 600°C lead to the same conclusion.

PA-26

USE OF LOW FREQUENCY AC MEASUREMENTS IN SOLID STATE ELECTROCHEMISTRY

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A new technique is described which allows the accurate measurement of the electrical impedance of an electrochemical system at very low frequencies.

The sinusoidal excitation signal and the response of the sample are compared over a single period, using a small on-line computer, by means of an algorithm based on the first term of the Fourier transformed signals. The relationships between the amplitudes and phases of the excitation and response are then calculated and displayed as a complex impedance.

Combined with more conventional high frequency measurements, this technique has given a total available frequency range of from 1MHz down to 5×10^{-4} Hz. This expanded capability greatly simplifies the analysis of the frequency dispersion of the impedance; the low frequency information being particularly desirable for the study of interface phenomena.

Examples of the application of this technique include studies of the ionically blocking electrode/solid electrolyte interface (e.g. Au/PbF_2) [1] the quasi-reversible interface (e.g. Li/Li_3N) and a study of the kinetics of the electrochemical injection of lithium into thin tungsten trioxide films. In this last example, in addition to giving information about the kinetics of the interface charge transfer reaction, solution of the diffusion equations for the appropriate finite boundary conditions correctly predicted the form of the impedance at very low frequencies, and allowed the determination of the chemical diffusion coefficient of lithium and the thermodynamic enhancement factor as a function of lithium activity in Li_yWO_3.

[1] C. Ho, Y-W. Hu, I. D. Raistrick and R. A. Huggins, J. Electroanal. Chem. 77, 319 (1977).

FOUR PROBE AC CONDUCTIVITY MEASUREMENTS FOR FAST ION CONDUCTORS*

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Ionic conductivity measurements are usually carried out with audio frequency ac in order to avoid polarization effects caused by partial blocking of the ions at the electrodes. A capacitance bridge with decade resistors is convenient for this purpose, but the usual 2 or 3 terminal measurements do not allow for lead wire corrections, which cannot be neglected for sample resistances as low as a few ohms.

Hence a 4 probe technique has been developed for use with a shielded transformer arm capacitance bridge. The principle is similar to the dc Mueller method for a platinum resistance thermometer: two balances are made, with the bridge connections reversed for the standard and sample resistances. The average of the two readings gives the sample resistance with all lead resistances completely eliminated, and the difference gives the lead resistance correction for future reference. Thus the method retains all of the advantages of shielded bridge techniques while at the same time automatically correcting for lead resistances.

The method has been used for measurements at high temperatures on AgCl and AgBr,[1] where the conductivity for AgBr rises to 1 $\Omega^{-1}cm^{-1}$ near the melting point! It should prove valuable for other fast ion conductors with comparably large conductivities, and experiments are in progress in connection with low temperature diffusion measurements on Ag-beta-alumina.

*Work supported in part by the U.S. Department of Energy

[1] R. J. Friauf, J. Physique 38, 1077 (1977); K. J. Kao and R. J. Friauf, to be published.

PA-28

RESOLUTION OF MULTICOMPONENT IMPEDANCE DIAGRAMS*

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Complex impedance (or admittance) diagrams usually exhibit more than one semicircle, and resolution of these semicircles is needed to determine the electrochemical parameters of the cell under investigation. Semicircles with relaxation frequencies differing by less than a factor of 100 overlap significantly, and when this factor drops below 10 the resulting diagram may appear to the eye to be a single semicircle. Similar overlapping may be observed between semicircles and Warburg-like straight lines.

A simple method, practicable with small desktop computers has been developed to confirm the existence of two components, to separate them accurately, and to determine their characteristic parameters: real intercepts (Z_i), relaxation frequencies (ω_0) and depression parameters (α).

The calculation is based on a determination of the curvature-center locus. Then, a $\ell n\, u/v = f\,(\ell n\, \omega)$ diagram over an appropriately selected frequency range is utilized leading to a first approximation to one of the components. The difference between the experimental and the first approximation is calculated, and the second component is thereby estimated. The calculation is iterated until the intermediate Z value is stable within a few percent. Two procedures are described to reduce the number of iterations required after the initial curve fitting.

*Supported by the National Science Foundation.

[1] On leave from E. N. S. d'Electrochimie et d'Electrométallurgie de Grenoble, Domaine Universitaire, 38401 St. Martin d'Héres, France.

PA-29

THE METAL SILVER-LIQUID INTERFACE: OXIDE PROPERTIES FROM REFLECTANCE AND SCATTERED LIGHT SPECTROSCOPY*

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Electrochemically oxidized silver foils have been examined using a reflectance and scattered light spectroscopy (termed RASCAL spectroscopy). The reflectance of both quasi-equilibrated silver oxide at an aqueous potassium hydroxide-metal interface and of oxide residue on metal in air have been examined in the 1 to 5 eV photon energy range. The effect on the metal reflectivity due to unintentional inhomogeneous oxide formation is discussed. An oxide coverage will reduce the metal reflectance most strongly in the free-electron energy region near the screened plasma frequency and has been observed to broaden the surface plasma resonance of the underlayer.

In contrast, the contribution to the reflectance of an intentionally formed oxide overlayer may be separated from that of the silver. Under the assumption that the scattering contribution of the oxide-covered metal can be made small, the differential reflectance between oxidized and clean metal foils may be used to determine the approximate optical constants of the overlayer. These parameters have been determined in our range of experimental data by using a modified form of Kramers-Kronig analysis.

Scattering contributions due to inhomogeneous oxide residues are shown. Information thus obtained may be used to estimate the distribution of oxide nodule sizes at the metal boundary. Such experiments have been compared to direct electron microscopy of the residues on the same surfaces.

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PA-30

MIXED IONIC AND ELECTRONIC TRANSPORT IN THORIA ELECTROLYTES*

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Thoria (ThO_2) is one of a number of oxides which exhibits fast oxygen ion transport at elevated temperatures when doped with di or tri valent cations (notably Y_2O_3). Though both pure and doped thoria are characterized by a predominantly p-type electronic conductivity at P_{O_2}'s $> \sim 10^{-5}$ atm, ionic conduction is found to predominate at reduced pressures making thoria the material of choice for oxygen sensors operating under highly reducing conditions.

To obtain adequate information concerning ionic and electronic generation and transport (of which little exists for the latter) in thoria electrolytes and to test the hypothesis that variable valent impurities limit the applicability of such probes, a series of electrical conductivity and ionic transport measurements have been performed on thoria doped with varying amounts of substitutional cerium. Increasing levels of cerium lead to increasingly larger "n-type" contributions at reduced P_{O_2}'s ultimately leading to the disappearance of the "ionic plateau". Our analysis of these and related data indicate that in contrast to conventional wisdom, the P_{O_2} dependent conduction at reduced pressures is predominantly ionic rather than electronic. Values for parameters controlling defect generation and transport are reported for the first time.

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PA-31

IONIC CONDUCTIVITY OF HIGHLY DEFECTIVE OXIDES

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The variation of conductivity of highly defective oxide solid solutions (e.g. those of $Th\,O_2$ and $Zr\,O_2$ with $Ca\,O$ and $YO_{1.5}$) with additive concentration shows a peak at about 12-18% of the dopant (concentration c). We suggest here a simple explanation which concentrates on the environment of a diffusing oxygen vacancy $V_0^{\cdot\cdot}$. For example, if $V_0^{\cdot\cdot}$ has as its nearest neighbour one or more Ca^{2+} ions (probability $(1-p_1(c))$) , it will be bound or at least be strongly impeded in its diffusion. Similarly because of strong vacancy repulsion we include only those configurations (probability $p_2(c)$) in which two vacancies are <u>not</u> nearest neighbours. The probabilities $p_1(c)$ and $p_2(c)$ are computed in the simplest independent site statistical approximation. We find that $c_{eff} = c\ p_1(c)\ p_2(c)$ has a peak at ~13% for the MO_2 - $M''O_{1.5}$ system and at ~16% for the MO_2 - $M''O_{1.5}$ system, in agreement with experiment. The general shape of $\sigma(c)$ vs. c is also in agreement with experiment, though the falloff for large c is steeper than calculated. A number of refinements are discussed.

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PA-32

THE RELATION BETWEEN THE THERMOELECTRIC POWER AND THE FAST IONIC CONDUCTION IN δ-Bi_2O_3.

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The high temperature δ-phase of Bi_2O_3 can be considered as a highly defective fluorite phase, with an existence range between 729 and 824 degrees C. This phase shows fast ionic conduction of the order 1 $\Omega^{-1}cm^{-1}$. Oxygen ions are the mobile charge carriers. (transport number $\approx$ 1). According to literature the existence range of the δ-phase can be extended to lower temperatures e.g. by addition of rare earth oxides. However these 'δ-phase materials' exhibit very poor ionic conduction at these lower temperatures.

The thermoelectric power is shown to be a very sensitive tool for studying the transport properties of these materials. When measured as a function of temperature and partial oxygen pressure it gives direct information on the electrode reversibility and the transported entropy. Furthermore it is very sensitive to an electronic contribution to the conductivity and can therefore be used to check the ionic character.

A combination of the experimental data concerning the thermoelectric power and theoretical considerations on the partial entropy of the oxygen ions in δ-Bi_2O_3 gives a very low value for the heat of transport. It is shown that the reported agreement between values of the heat of transport and the activation energy for the electrical conduction in various fast ionic conductors is not firmly sustained by theory. Moreover this very low value might very well be characteristic for fast ionic conductors.

PA-33

NMR STUDY OF SODIUM ION MOTION IN β" ALUMINA

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The temperature dependences of the nuclear quadrupole coupling constant, e^2qQ/h, and the asymmetry parameter, η, have been measured for ^{23}Na in single crystal M_gO stabilized β"-alumina.

Over the range of temperature studied, the rotation pattern data are consistent with a model which invokes rapid sodium ion motion among trigonally related sites in the conduction plane.

The coupling constant is 3.4 MHz (±2%) over the temperature range, while the asymmetry parameter varies nearly linearly from 0.47 at 295K to 0.85 at 219K.

The results of this work are qualitatively similar to those found by Chung et al.[1] For ^{23}Na in β-alumina.

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* Permanent address: Naval Air Development Center, Warminster, PA.

[1] I. Chung, H. Story, and W. Roth, J. Chem. Phys. 63, 4903 (1975).

PA-34

STUDY OF ANOMALOUS Na IN Na_2O ENRICHED BETA-ALUMINA

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Pulsed and CW NMR techniques were used to investigate the ^{23}Na motion and relaxation behavior of the anomalous Na typically found[1] in Na_2O enriched Na beta-aluminas ($1Na_2O\cdot5.72Al_2O_3$). The results show that the spin lattice relaxation time (T_1) for the anomalous Na is about 100 times longer than the T_1 associated with the normal Na. T_1 = 20 ms at 300 K with an activation energy of 0.13 eV. The observed linewidth ($T_2^* \approx 35$ μs) of the anomalous Na does not seem to undergo motional narrowing between room temperature and 75 °C. Spin echo experiments show that the line is inhomogeneously broadened at room temperature ($T_2 \approx 600$ μs). Coarse grained single crystal powders of Na beta-alumina ($1Na_2O\cdot9Al_2O_3$) exhibited both anomalous and normal Na responses after attempts to promote vapor phase Na_2O enrichment. In addition to introducing the anomalous Na response this treatment also increased the magnitude of the coupling constant of the normal Na to values consistent with Na_2O enrichment. Our conclusion is that the anomalous Na must be incorporated within the beta-alumina structure.

[1] R.R. Dubin, H.S. Story, R.W. Powers, and W.C. Bailey, Mat. Res. Bull., Vol. 14, 1979.

Na^{23} NMR AND TWO-DIMENSIONAL DIFFUSION IN β-ALUMINA*

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We discuss the NMR data of Na^{23} in β-alumina with a formalism which takes into account the two-dimensional (2D) character of the system. Since the electric field gradient (e.f.g.) at the Na^{23} position has the symmetry created by a planar distribution of charges, the e.f.g. tensor can be written in terms of $A = \Sigma_j\, e_j/r_j^3$ and $B = \Sigma_j\, e_j\, \exp(2i\Phi_j)/r_j^3$. (Here $\vec{r}_j(r_j,\Phi_j)$ is the planar vector connecting the nucleus with the charge e_j.) The correlation functions <A(t)A(0)> and <B(t)B(0)> and their spectral densities are evaluated: 1) by assuming that sodium moves in the plane following a 2D-diffusion equation and 2) by neglecting the terms involving correlation between different charges. The most interesting feature of this 2D-model is that at long times one has: $\langle A(t)A(0)\rangle \propto t^{-1}$. This fact is directly confirmed by the changes in width of a satellite line with temperature. Moreover, the model gives an accurate description of the observed[1] temperature and frequency dependence of the transition probabilities. The reasons for this agreement and the information given by NMR on the sodium motion in β-alumina are discussed.

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*Supported in part by Fondazione Della Riccia, Firenze, Italy, and by NASA.

[1] R. E. Walstedt, R. Dupree, J. P. Remeika, and A. Rodriquez, Phys. Rev. B15, 3442 (1977).

PA-36

NMR OBSERVATIONS OF Na IONIC DIFFUSION IN Na β"-ALUMINA AND NASICON*

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We measured the temperature dependence of the nuclear relaxation time T_1 at 24 MHz for ^{23}Na in dry powdered Na β"-alumina and in polycrystalline $Na_3Zr_2PSi_2O_{12}$ (NASICON). Both materials show a strongly asymmetric minimum in a plot of T_1 vs. $1/T$. We determined the activation energies from the T_1 data and obtained, for temperatures below the T_1 minima, activation energies which are about one third of those derived from data above the minima. The possibility that this asymmetry arises from cross relaxation effects between energy levels split by the quadrupolar interaction will be discussed. In particular, we found that modifying the pulse sequence used to measure T_1 can increase the slope of the low temperature T_1 data for Na β"-alumina.

For both Na β"-alumina and NASICON, the activation energy E_a determined from the high temperature side of the T_1 minimum tends to be slightly higher than published values derived from ionic conductivity. Since $\omega_0\tau \sim 1$ at the T_1 minimum, we can estimate the jump time $\tau = \tau_0 \exp(E_a/kT)$ and the attempt frequency $\nu_0 = \tau_0^{-1}$ using the high temperature value of E_a. We found $\nu_0 \sim 10^{13}\,\mathrm{sec}^{-1}$ for NASICON and $\nu_0 \sim 10^{14\pm1}\,\mathrm{sec}^{-1}$ for Na β"-alumina. This latter value is higher than $\nu_0 \sim 10^{11}\,\mathrm{sec}^{-1}$ found by Walstedt et al for Na β-alumina.[1]

Above the T_1 minimum in Na β"-alumina our observed lineshape corresponds to a second order quadrupolar broadened powder pattern of the central transition arising from field gradients not averaged out by the motion. Below the T_1 minima, we observed dipolar and quadrupolar defect broadening superposed on the lineshapes.

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*This work was supported by NFS grant #DMR 76-18966.

[1] R.E. Walstedt, R. Dupree, J.P. Remeika & A. Rodriquez, Phys. Rev. B15, 3442 (1977).

LOW TEMPERATURE STUDY OF ^{23}Na SATELLITE SPECTRA IN β-ALUMINA

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Details of the sodium ion motion (site exchange processes) in β-alumina have been obtained from analysis of first-order quadrupolar $^{3/2}$Na NMR spectra. Quadrupolar interactions were studied as a function of crystal orientation and temperature using a recently developed double resonance technique[1] which provides a sensitive, although indirect, means to obtain such first-order spectra. The experimentally determined electric field gradients have been compared with point charge calculations to aid in identification of the sodium sites, and temperature-dependent changes in the multiplet structure of the first-order sodium spectra have allowed characterization of the multiple-site sodium exchange processes present.

[1] M. Polak and R. W. Vaughan, J. Chem. Phys. 69, 3232 (1978).

PA-38

PHYSICAL CORRELATION EFFECTS IN THE LATTICE GAS*

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The lattice gas has long been of interest in connection with the modeling of solidification, adsorption, the behavior of interstitial solid solutions and now, more recently, superionic conductivity. Although the lattice gas is very simple in concept, the rigorous physics has proved, like the analogous Ising magnet, to be quite difficult of access. Computer simulation has played a key role in our understanding of the properties of the lattice gas. Recently, using computer simulation methods, the present authors revealed that for the *a priori* site equivalent lattice gas, the usual Nernst-Einstein equation must be modified by the factor (f_c/f_t), where f_c is the *physical* correlation factor and f_t is the *tracer* correlation factor.

In this paper we make use of the Onsager formalism of irreversible thermodynamics to show that (f_c/f_t) not only modifies the Nernst-Einstein equation it also modifies the Darken equation. This is a very interesting and illuminating result which underscores the importance and fundamental nature of f_c. Since we have previously developed simulation methods to calculate (1) the tracer diffusivity, (2) the drift mobility, (3) the chemical potential and, very recently, (4) the chemical diffusivity, we also present results of an "experimental" verification of the modified Darken equation.

*Work performed under the auspices of the Office of Basic Energy Sciences of the U. S. Department of Energy.

TEMPERATURE DEPENDENCE OF HAVEN RATIO IN FAST ION CONDUCTORS AND CORRELATION EFFECTS*

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A recent measurement of the Haven ratio H_R of β-alumina[1] shows a strong temperature dependence which cannot be explained in terms of random walk concept of ionic diffusion and conduction. On the other hand, an almost quantitative explanation of this effect can be given by a many body diffusion theory developed by the present authors[2] utilizing a very simple model of β-alumina. The temperature dependence of the Haven ratio in this case is due to a strong temperature dependence of the correlation effect of both the diffusion and the conduction as a result of the change of population of conducting ions among several kinds of available lattice sites by temperature and to a difference in the statistical nature of diffusion and conduction. Here the "correlation factor" is defined as the efficiency of the motion of ions with respect to that of random walk process. (In the limit of low vacancy concentration, the "correlation factor" of isotope diffusion thus defined is reduced to the well known correlation factor for the self diffusion). Since the correlation effect depends on the detailed nature of the geometry of the path of ions as well as the time sequence of motion of ions, the correlation effect is very sensitive to the structural changes such as the introduction of impurities, order-disorder transiton phenomena, and also to the frequency of conductivity measurements. Importance of the "correlation effect" in elucidating the conduction mechanism of fast ionic conductors is thus emphasized.

*Supported by NSF DMR 7621497

**Permanent address: Hughes Research Laboratories

[1] J. N. Mundy, Twenty-sixth Midwest Solid State Conference, Oct. 1978

[2] H. Sato and R. Kikuchi, J. Chem. Phys. 55 677 (1971)

PA-40

MODEL STUDIES OF MIXED-ION BETA-ALUMINAS[*]

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Recent results of NMR, Raman scattering, IR, diffusion and conductivity measurements on mixed-ion beta-aluminas reported in the literature have revealed several important phenomena in these systems. These include the preferential occupancy of particular kinds of sites for some ions and anomalies in conductivity due to ion mixing and to the presence of H_2O in the conducting plane. We have attempted to understand these phenomena with model calculations similar to those reported previously.[1] By including Coulomb, short-range repulsive, and polarization energy terms, the potential energies of various ion arrangements were calculated to determine the most stable configuration and the activation energies of diffusion. Our results for various monovalent and divalent cations as well as for water molecules in Li, Na, and K beta-aluminas have shown that the preferential occupancy of ion sites may be explained by potential energy considerations, and the anomalies in conductivity may be attributed to the effects of correlative motions of various ion pairs on the activation energies and to the blocking of conduction paths by impurity ions or water molecules.

[*] Research sponsored by the Division of Materials Sciences, U. S. Department of Energy under contract W-7405-eng-26 with Union Carbide Corporation.

[+] Guest scientist on leave from Fuji Photo Film Co., Tokyo, Japan.

[1] J. C. Wang, M. Gaffari, and Sang-il Choi, J. Chem. Phys. 63, 772 (1975).

PA-41

CORRELATION EFFECTS IN NON-STOICHIOMETRIC CRYSTALS: APPLICATION TO β"-ALUMINA*

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The correlated diffusive motion of atoms due to the presence of a large concentration of vacancies in non-stoichiometric crystals is investigated in terms of the encounter model. Within the framework of this model the correlation factor f is found to be equal to the ratio of the mean square displacement, $<d^2>_{enc}$, of the tracer in an encounter with a given vacancy and the mean number of correlated tracer jumps per encounter, Z_{enc}. Both $<d^2>_{enc}$ and Z_{enc} have been determined as functions of C_V by means of a computer simulation program for a vacancy diffusion mechanism of the Na^+ ions in sodium β"-alumina. The concentration dependence of the correlation factor thus obtained is compared with the Monte Carlo computer simulation results of Murch and Thorn[1] and with the theory of Sato and Kikuchi.[2]

For polycrystalline β"-alumina samples the ratio of the radio-tracer and charge diffusion coefficients (so called "Haven ratio") is determined and compared with the experimental results of Ormrod and Kirk.[3] Possible reasons for the very low values of H_R extracted from the experiments are discussed.

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*Work supported by the U.S. Department of Energy.

[1] G. E. Murch and R. J. Thorn, Phil. Mag. 36, 529 (1977).

[2] H. Sato and R. Kikuchi, J. Chem. Phys. 55, 677 (1971).

[3] S. E. Ormrod and D. L. Kirk, J. Phys. D 10, 1497 (1977).

ABSTRACTS

of

CONTRIBUTED PAPERS

Poster Session PB

IONIC CONDUCTIVITY IN LITHIUM OXIDE-FLUORIDE GLASSES*

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Li^+-rich borate glasses, containing lithium oxide, lithium fluoride, and other lithium salts exhibit high electrical conductivities at elevated temperature (1.5×10^{-3} Scm^{-1} at 200°C). The ionic conductivities σ and the activation energies E_σ [determined from $\sigma = \frac{A_\sigma}{T}\exp(-E_\sigma/kT)$] were investigated as a function of $F^-/O^=$ ratios in these glasses. The results indicate an increase in conductivity and a decrease in activation energy with an increase in LiF content in the system. The glass transition temperatures T_g also increase as $F^-/O^=$ ratio increases. These results are interpreted in terms of changes in glass structure with composition.

The influence of the thermal history (annealing temperature and rate of cooling) on ionic conductivity was studied and correlated with the T_g's dependence on the heating or cooling rate $|q|$. This dependence is given by $\frac{d \ln |q|}{d (1/T_g)} = - \frac{\Delta h^*}{R}$ where Δh^* is the activation enthalpy for relaxation times controlling the structural enthalpy or volume relaxation.

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*Supported in part by NSF-MRL Grant No. DMR77-23798.

PB-2

^{11}B LINESHAPE AND SPIN-LATTICE RELAXATION IN $(AgI)_x(Ag_2O\ B_2O_3)_{1-x}$ AMORPHOUS SUPERIONIC CONDUCTORS

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This paper shows that detailed information can be obtained on the mechanism responsible for the fast ionic transport in $(AgI)_x(Ag_2O\ B_2O_3)_{1-x}$ amorphous compounds by analyzing the ^{11}B NMR response. At room temperature, dc conductivities of $\sim 10^{-2}\ \Omega^{-1}\ cm^{-1}$ have been observed(1) for $x<.2$, $x>.8$, in the amorphous phases of these compounds. The ^{11}B lineshape shows almost no dependence on the AgI content and indicates that all borons are tetrahedrically coordinated to four oxygens. The spin lattice relaxation times (T_1) of ^{11}B have been measured in the range 5°-450°K for various AgI contents (from $x=0$ to $x=.8$). All the T_1 vs. T curves go through a minimum, the position of which depends on both the composition (x) and the Larmor frequency. It is demonstrated that the minima are caused by activated fluctuations of the BO_4 groups and that this motion is related to the high ionic conductivity of the glasses. The coupling between the motion of the borate units and the Ag^+ diffusion is treated by introducing an exchange-type model Hamiltonian. It has been found that neither the ionic conductivity nor the ^{11}B NMR response appreciably change when iodine is substituted with bromine. This fact agrees nicely with the predictions of the exchange model and suggests that it could explain the conductivity of other amorphous systems. The importance of these findings from the technological point of view is briefly commented.

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ROLLER QUENCHING FOR PREPARING HIGH CONDUCTIVITY GLASSES

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By using a rapid quench technique such as roller quenching,(1) it is possible to convert a large variety of melted compositions into the vitreous state even although they do not contain any glass-formers such as SiO_2, P_2O_5, B_2O_3, etc. Cooling rates as high as 10^7 degrees per second are readily achieved. The quenched glasses are typically thin flakes 5 mm by 10 mm by 10 μm thick.

Examination by x-ray diffraction and by differential thermal analysis demonstrates the presence of glass by the absence of diffraction peaks and by the presence of glass transitions and crystallization exotherms, often with the first crystalline phase to form being a new metastable phase.

Preliminary studies(2) in the systems of Li_2O-Na_2O-K_2O with Ta_2O_5-Nb_2O_5, using only the stoichiometric meta compositions such as $LiNbO_3$, indicated that highest ionic conductivities(3) as high as 10^{-5} $(\text{ohm cm})^{-1}$ occurred with the Li compounds. Anomalous dielectric behavior with dielectric constant peaks over 3×10^5 was also observed.(4)

Accordingly a more widespread survey of Li-containing oxide compositions with variations both in the added cation as well as in the stoichiometry was initiated. The preparation technique and the occurrence of glasses and high ionic conductivity compositions will be described.

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PB-4

CROWN ETHER SOLID ELECTROLYTES*

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Complexes of Lithium, fluoride, chloride, bromide, and iodide with dibenzo-18-crown-6 have been formed by dissolving stoichiometric quantities of crown ether and the lithium halide in methanol and slowly evaporating the solvent. The solid was then compressed into a pellet at 40,000 psi and its ac conductivity measured at room temperature using an industrial instruments conductivity bridge at a frequency of 1000 Hz. The conductivities at room temperature indicate that the salts are anionic conductors rather than cationic conductors and that, of the four complex halides, dibenzo-18-cr-6 LiCl is the best conductor.

*Supported by Faculty Research Committee Bowling Green State University

PB-5

CHARACTERIZATION OF HEAT TREATMENT INDUCED CHANGES IN Li-Na BETA ALUMINA SINGLE CRYSTALS

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Single crystals of lithium-sodium beta alumina with 50% to 95% substitution of Li^+ for Na^+ were annealed in air and in vacuum at temperatures up to 1000°C. The specimens were examined before and after each heat treatment by pulsed NMR, Raman scattering, infrared absorption, and x-ray diffraction. After annealing at 600°C, the two original Raman bands at 393 and 370 cm^{-1} due to $^7Li^+$ vibrations merged into a single peak centered at 380 cm^{-1} accompanied by a narrowing of spinel block phonon bands at 427 and 322 cm^{-1}. Annealing at 1000°C caused a sharpening of the Li^+ band, but no further changes were observed in the shape of neighboring phonon lines. The 1000°C annealing introduced a broad ^7Li NMR response and substantially reduced narrow line ^7Li intensity. This confirmed similar changes reported in heat treated sintered Li-Na beta ceramics. X-ray Laue patterns showed that strain was induced by heat treatment; however, the original crystal symmetry remained unchanged. The present results suggest that the thermal induced changes observed in the NMR and Raman spectra of lithium ions are due to diffusion of lithium out of the conducting plane and into the spinel-block.

*Guest scientist on leave from Fuji Photo Film Company, Tokyo, Japan

†Operated by Union Carbide Under Contract No. W-7405-eng-26 With U.S. Department of Energy

PB-6

LITHIUM MOTION AND ACTIVATION IN Li-Na BETA ALUMINA SOLID ELECTROLYTES

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Spin lattice relaxation times (T_1) and observed line-widths (T_2^*) for ^{7}Li in single crystal Li-Na beta-alumina were determined by pulsed NMR as a function of temperature and rotation angle. The specimens were prepared by ion exchange techniques and had a final Li^+:Na^+ ratio of 3:1. Both T_1 and T_2^* showed a noticeable dependence on rotation angle. Spin echoes were not detectable at room temperature; however, they were observed at 155°K indicating inhomogeneous line broadening at low temperature. As in the case of previously studied[1] polycrystalline sintered specimens motional narrowing occurred throughout the investigated temperature range (150°K to 500°K). Activation energies for Li^+ hopping are calculated from the T_1 vs. temperature results and are compared to reported results on Li-Na beta-alumina ceramics. In addition, similar measurements are underway with Li^+ substituted single crystal Na beta" alumina. These results will also be reported and compared to those obtained from the Li^+ substituted Na beta alumina.

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DISTRIBUTION OF IONS IN MIXED β- ALUMINA*

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It has been known that beta-alumina crystals with mixture of monopositive ions in place of sodium ions exhibit rather interesting properties. Li-Na beta-alumina is an example. Since considerable amount of experimental data exist for Na-K beta-alumina with varying relative concentrations of two ions, we carry out a theoretical study of this system. Our work is based on Kikuchi's theory of cooperative phenomena. It is assumed that 5 species of "particles" exist: Na^+, K^+, Na^+-Na^+, K^+-K^+, and Na^+-K^+. Minimization of free enrgy yields a set of coupled nonlinear equations for the relative concentrations of these species. Solutions of this set of equations yield the relative concentrations as functions of energy parameters and the ratio of Na^+ and K^+ ion concentrations. The theory is applied to the analysis of existing experimental data.

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PB-8

IONIC CONDUCTIVITY AND RAMAN SPECTRA OF Na-Li, K-Li, and K-Sn BETA-ALUMINA*

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The ionic conductivity, σ, and Raman spectra of Na-Li, K-Li, and K-Sn β-alumina crystals were measured in order to understand the mechanism of mixed-ion conduction. In mixed Na-Li crystals we found an approximately linear relationship between $\log(\sigma T)$ and $1/kT$. However, the slope of this graph was discontinuous at a temperature which decreased with increasing Li^+ concentration. A model based on pair-cation motion has yielded a theoretical fit to these data. It was observed that, at 300 K for example, the conductivity of a crystal with composition $Na_{0.82}Li_{0.18}\beta\text{-}Al_2O_3$ was about one-fourth that of pure $Na\beta\text{-}Al_2O_3$, while the conductivity of $K_{0.80}Li_{0.20}\beta\text{-}Al_2O_3$ was more than three orders of magnitude lower than that of pure $K\text{-}\beta Al_2O_3$. Features observed in the Raman spectra Li-Na, Li-K, and K-Sn β-aluminas were attributed to paired- and single-ion vibrations.

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SODIUM ION CONDUCTORS - NASICON AND Na-ß-ALUMINA

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The purpose of this paper is to compare the behaviour of the two sodium-ion conductors NASICON ($Na_3Zr_2Si_2PO_{12}$) and Na-ß-alumina. Both materials were in the form of small sintered discs and the ß"-form of Na-ß-alumina was stabilised by the addition of either magnesium or lithium oxide. The impedance of the sinters has been measured between 25°C and 400°C and the complex plane impedance diagrams analysed in terms of the ideal equivalent circuit for a sintered material. This allowed the separation of the bulk ionic conductivity and the intergranular resistivity. The temperature dependence of these components is presented and compared to literature values. It is shown that, with these samples, the dc conductivity is dominated by the ionic motion in the bulk of the material.

The stability towards sodium was also checked and the behaviour with sodium electrodes measured.

PB-10

SLOW TRANSIENT PHENOMENON IN Y-DOPED CeO_2*

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Four-probe dc conductivity measurements on some ceramic Y-doped CeO_2 specimens exhibit a slow transient voltage under constant current conditions. This transient has the characteristics of a diffusion-controlled process, with diffusion coefficients typical of solid state transport. The most probable mechnanism appears to involve coupled diffusion of electrons and oxygen vacancies, as earlier proposed in such materials by Fouletier et al.[1] and Wang and Nowick[2]. The effect appears to be sensitive to the microstructure and may not be intrinsic.

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*Partially supported by the Department of Energy

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ELECTRICAL CONDUCTION IN THE CUBIC FLUORITE PHASE IN THE SYSTEM ZrO_2 - $YO_{1.5}$ - $TaO_{2.5}$

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The cubic fluorite phase was found to exist in approximately a triangular region in the system ZrO_2-$YO_{1.5}$-$TaO_{2.5}$ $(ZrO_2)_{32}$ $(YO_{1.5})_{68}$ and $(ZrO_2)_{47.5}$ $YO_{1.5})_{36.5}$ $(TaO_{2.5})_{16.0}$. In these solid solutions anion vacancy concentration increases with $YO_{1.5}$ and decreases with $TaO_{2.5}$ additions. Thus $YO_{1.5}$ is a vacancy generator and $TaO_{2.5}$ is a vacancy annihilator. The lattice parameters of these solid solutions increase while Y^{3+} replace Zr^{4+} ions and decrease while Ta^{5+} replace Zr^{4+} ions. The electrical conductivity of the ternary compositions is independent of oxygen partial pressure in the range $p_{O_2} = 1$ to 10^{-22} atm at 600 to 1200°C indicating the essentially ionic nature of conductivity. Temperature variation of electrical conductivity follows the Arrhenius relationship indicating a single conduction mechanism in the range of composition, temperature and p_{O_2} employed here. In a series of compositions with a fixed anion vacancy concentration which was achieved by matched additions of $YO_{1.5}$ and $TaO_{2.5}$ the isothermal conductivities vary only slightly with ZrO_2 content. On the other hand isothermal conductivity varied in a complex manner with anion vacancy concentration when ZrO_2 or $TaO_{2.5}$ were fixed. These results are interpreted in terms of ionic ordering in the ternary system. It has been shown that the anomalous conductivity behavior connected with ionic ordering in the binary system ZrO_2 - $YO_{1.5}$ is projected into the ternary system. The role of size and charge of the competing dopantions on the electrical behavior is examined.

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PB-12

IONIC CONDUCTION IN DOPED ZIRCONIA

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The ionic conductivity of zirconia doped with aliovalent metal oxides, Zr(M)O_{2-x} ($x > \sim 0.08$), decreases with increasing anion vacancy concentration while the activation energy becomes larger, typically changing from 0.9 eV near $x = 0.10$ to 1.5 eV near $x = 0.2$. Plots of σT vs $1/T$ for Zr(M)O_{2-x} with different dopant concentrations x therefore always show a trend towards convergence at higher temperatures, i.e. toward a vacancy concentration independent conductivity σ_o at temperature T_o.

The analysis of such data on the basis of the conventional expression $\sigma T = A(x)\exp(-E(x)/kT)$ shows that the pre-exponential factor itself is an exponential function of E (or of x since $E \propto x$), $A(x) = \sigma_o T_o \exp(-E(x)/kT_o)$. This relation deviates strongly from $A(x) \propto x^n$ with $n \sim 1/2$ that is required for theoretical models of ionic conduction with vacancy-impurity association.

The significance of the empirical relationship and its possible interpretation will be discussed. It will be shown that the ionic conductivity in doped zirconia is described by $\sigma = \sigma'\exp{-\Delta G(x)/kT}$. σ' is the conductivity calculated with inclusion of nearest neighbor defect interaction; it is modified by $\exp{-\Delta G(x)/kT}$ where $\Delta G(x)$ is a composition-dependent free energy.

OXYGEN-ION CONDUCTIVITY AND DEFECT STRUCTURE OF CeO_2 DOPED WITH CaO AND Y_2O_3*

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Little is known about the detailed defect structure of the fluorite-type oxides which are good oxygen-ion conductors. Toward this objective, we have measured the ac conductance and parallel capacitance of various doped ceria samples as functions of frequency and temperature from 20 Hz to 13 MHz. Through the use of complex impedance plots, the true lattice conductivity can be separated from electrode polarization and from grain-boundary effects. The dependence of lattice conductivity on temperature and dopant concentration has been studied, particularly at low dopant concentrations.

In the case of CaO-doped CeO_2 the predominant defect is the Ca''-$V_O^{\cdot\cdot}$ pair in the nearest-neighbor configuration. The activation enthalpy of the lattice conductivity is nearly a constant (0.92 eV) over the range from 1 to 15 mole % CaO.

The Y_2O_3-doped CeO_2 shows very different results. First, σ as a function of Y_2O_3 concentration goes through a sharp maximum near 4 mole % Y_2O_3 while the activation enthalpy increases abruptly from a value of 0.78 eV for concentrations less than 4% Y_2O_3, to values greater than 1.0 eV. Here one $V_O^{\cdot\cdot}$ compensates for every two Y^{3+} ions but cation immobility below 1000°C presents the formation of completely compensated defects. By analysis of these conductivity results together with complementary data for anelastic and dielectric relaxation, a model is developed for the defect structure at low concentrations of Y_2O_3.

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[1] Now at General Electric Res. Dev. Center.

[2] Now at IBM Components Div., Fishkill.

PB-14

ELECTRICAL CONDUCTIVITY IN CERAMIC SOLID SOLUTIONS OF ZrO_2-$LnO_{1.5}$, WITH Ln=Gd, Nd.

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The electrical conductivity in ceramic solid solutions of ZrO_2 substituted with $GdO_{1.5}$ or $NdO_{1.5}$ is investigated at temperatures between 500 and 750°C. Complex admittance, DC and EMF (concentration cell) techniques are used for analysis.

In these systems an ordered pyrochlore phase is present around 50 at% Gd (or Nd) and this phasestructure is closely related to the defect fluorite structure. Bulk conductivities are separated from grain boundary conductivities by complex plane analysis and agree with our measurements on single crystals. Bulk conductivities are not influenced by grain size in the range between 0.2 and 25 μm.

The conductivity as a function of Gd concentration reaches a maximum at the composition $Gd_2Zr_2O_7$. The conductivity value at the maximum is about the same as those mentioned in literature for the maximum conductivity at low Gd concentration. Contrary to the Gd substituted case, the conductivity at the composition $Nd_2Zr_2O_7$, reaches a minimum value.

In both substituted ZrO_2 systems the preexponential factor σ_o as well as the activation energy of conductivity decrease with increasing substitute concentration, reaching minimum values at the pyrochlore composition $Ln_2Zr_2O_7$. The ionic transport number τ_i, determined between oxygen and air is one in the system ZrO_2-$CdO_{1.5}$. In the system ZrO_2-$NdO_{1.5}$ τ_i starts to decrease from one at Nd concentrations above 45 at%.

The conductivity results will be discussed in terms of defect and ordering parameters.

EXPERIMENTAL STUDY OF IONIC CONDUCTIVITY IN Cu_3VS_4 (SULVANITE)

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The mixed transport properties of Cu_3VS_4 were reported, and the ionic contribution to the conductivity was deduced from the observed "polarization" of the crystal. The ionic contribution to the conductivity appears to be appreciable (1).

In attempting to determine the ionic conductivity, a blocking electrode measurement was performed. All experiments were performed under argon, utilizing a cell consisting of a sandwich type arrangement of Cu/Cu^+ electrolyte (2) / Cu_3VS_4 / Cu^+ electrolyte / Cu.

Measurements have been performed as a function of temperature at various current densities and geometric arrangements in order to eliminate polarization problems. Results of these measurements are compared to those previously obtained for total transport. A complementary study of a cell with a Cu/Cu_3VS_4 /S+C arrangement was examined in order to determine the transport number.

The discussion of the results will include correlations to the structure and effects of non stoechiometry on electronic and ionic conductivity.

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PB-16

THE PHYSICAL AND CHEMICAL PROPERTIES OF COPPER β-ALUMINA

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Sodium β-alumina exhibits ion exchange with the cations of many molten salts. Copper(I) β-alumina has been prepared by the electrolysis of a molten cuprous chloride plus copper mixture across a single phase sodium β-alumina. The resulting β-alumina was characterized for lattice parameters and phase content using an X-ray method and both the ionic and electronic conductivities were measured using both solid and molten salt electrodes.

An e.m.f. technique, incorporating the copper β-alumina solid electrolyte, was then used to measure the thermodynamics of the copper and tin solutions of copper-tin alloys in the range 800K to 1100K in the mole fraction $X_{Cu} = 0.17$ to $X_{Cu} = 0.74$. The results obtained were in excellent agreement with previous determinations.

GIANT DECREASE OF Cu_3VS_4 ELECTRONIC CONDUCTIVITY IN IONIC SOLUTION

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Cu_3VS_4 is a mixed conductor in which a small number of interstitial Cu^+ ions can move with high mobility through crystallographic channels and partially compensate the basically p-type electronic semiconductor.[1]

We report a large decrease of electrical conductivity observed in Cu_3VS_4 monocrystalline samples when immersed in ionic solution, in particular in acid, at room temperature : We observe changes of up to six orders of magnitude in half-an-hour in HCl 0.1 N. The decrease is achieved after a time depending on the nature and concentration of the solution, sample size and preparation, but the final conductivity, of the order of $10^{-6}\ \Omega^{-1}\ cm^{-1}$ is the same for all the samples and solutions which have been tried.

We show that this change is a change of the electronic conductivity in the bulk of the material. In the final state the electronic and ionic conductivity may be of the same order of magnitude. We believe that this conductivity decrease is due to a compensation of the semiconductor by cations $H^+(H_3O^+)$ in the case of acid, which enter the sample and diffuse through the crystallographic channels. The same number of electrons fill the empty states of the valence band causing a decrease of the number of conducting holes. According to this model, in the final state, the semiconductor is completely compensated and we observe the intrinsic conductivity of the material. As in the case of "normal" Cu_3VS_4 it is possible to decompensate the semiconductor by applying a D.C. current of intensity larger than 1 μA.

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PB-18

THE ELECTRICAL CONDUCTIVITY AND CRYSTAL STRUCTURES OF POLYAMINE IODIDE/SILVER IODIDE SOLID ELECTROLYTES

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During the past decade there has been considerable interest in AgI-based solid electrolytes because of their anomalously high ionic conductivity at room temperature. In these electrolytes conduction occurs by the migration of Ag^+ ions through continuous channels of face-shared I^- polyhedra (generally tetrahedra).

This paper reports the ionic conductivity of five quaternary polyamine iodide/silver iodide solid electrolyte systems (for example N,N,N,N',N',N'-Hexamethyl-1,2-ethylenediamine diiodide/AgI). Conductivity maxima of these double salt systems vary from 0.023 to 0.109 $\Omega^{-1}cm^{-1}$ at 20°C for electrolyte phases containing between 91.5 and 97.0 $^m/o$ AgI.

A description of the crystal structures of six individual phases isolated from these solid electrolyte systems is given. On the basis that a structure must contain continuous channels of face-shared I^- polyhedra for it to be regarded as a solid electrolyte, each of the six structures can be classified either in terms of representing a non conducting phase, a two-dimensional or a three-dimensional solid electrolyte.

TRANSIENT CURRENT IN THE CELL, ⊖ Cu|CuI|GRAPHITE ⊕

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When the cell is at steady state under an applied potential E_1, and a new voltage E_2 is supplied abruptly, where $E_2>E_1$ and both are below the decomposition potential, there is a transient current due to the redistribution of electronic carriers and movement of ions. The theoretical curve of hole currents versus time, which is obtained by using Wagner's formula indicates an exponential increase form an initial steady state current to a final value. However, the experimental plots of log current versus time show a decay curve and has an inflection point.

An initial ionic transport establishes a composition gradient through the iodine 1); because the graphite electrode suppresses the ionic current. A potential distribution in the slab of CuI is given by, 1)
$\zeta(x) = -\frac{kT}{e}\ln[1-(\frac{L-X}{L})(1-e^{-\frac{eE_1}{kT}})]$, where L is the length of the sample, F the Faraday constant and X the distance from the graphite electrode. The potential variation (E_1-E_2) at $x=0$ produces a high density domain of ionic carriers N_i; corresponding to the activity of metallic copper, $a_{cu}=e^{-\frac{(E_1-E_2)F}{RT}}$. These ionic transport is expressed by the continuity equation. The solution is written by $\delta N_i(x,t)=\frac{N_i}{\sqrt{4\pi Dt}}\exp[-\frac{(x-\mu_i E_2' t)^2}{4Dt}-\frac{t}{\tau_i}]$ where D is the diffusion constant of ions, μ_i the ionic mobility and τ_i the effective lifetime for ionic carriers. The solution suggests that the ionic domain continuously moves through the cell. The drift mobilities of copper ion in CuI are obtained from the inflection point, being in good agreement with the experiments by the other method.

1) M.H.Hebb, J.Chem. Phys. 20 185 (1952)

PB-20

HOLE CURRENT-VOLTAGE CHARACTERISTICS IN ⊖ Cu|CuI|GRAPHITE ⊕

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The steady state hole current in the cell, Cu|CuI (CuCl)|graphite(+), as a function of the applied voltage E is experimentally obtained to be $I_{\oplus} = \frac{RTA}{LF} \sigma^{\circ}_{\oplus} [\exp(\frac{EF}{nRT})-1]$ where $\sigma^{\circ}_{\oplus}$ is the conductivity due to holes in CuX, L the thickness of a sample, A the cross-sectional area, F the Faraday constant and n an empirical factor. At lower applied voltages, $n \simeq 1$ for various temperatures. However, at higher voltages of $E > \sim 0.2V$ and below the decomposition potential, the values of n varies from 1.4 to 2.9, depending upon the temperature.

An initial transient ionic transport establishes a composition gradient through the iodide, because the graphite electrode suppresses the ionic current. A potential distribution in the slab is given by[1)] $\zeta(x) = -\frac{kT}{e} \ln[1-(\frac{L-X}{L})(1-e^{-\frac{eE}{kT}})]$. Then, the potential drop is concentrated in a thin layer at the graphite electrode. When the electric field becomes sufficiently high in the thin layer, it may be expected that a tunneling process is involved. In the case that the factor n changes largely for all types of heterojunctions, the forward V-I characteristics due to tunneling over a range of temperatures is empirically given by the equation,[2] $I = I_0 \exp(\frac{T}{T_0}) \exp(\frac{V}{V_0})$ (1). In our experiments, the relationship of $E_q l$ is satisfied at the constant fields of 0.34, 0.32, 0.30 and 0.28eV for CuI, (0.7, 0.68, 0.66; 0.64 and 0.62V for CuCl).

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VOLUME OF ACTIVATION FOR FAST IONIC CONDUCTION - A PROPOSITION FOR SOLID AND MOLTEN SALTS

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Basing on reasoning of the absolute rate theory we propose a phenomenological approach to the volume of activation in cases where the energy of activation is comparable with the mean thermal energy. If the temperature of absolute zero is the starting level, the volume of activation ΔV_i^* at temperature T for a mobile ion should be equal:

$$\Delta V_i^* = \frac{V_{T_i} \alpha_i T}{1 + \alpha_i T} \qquad (1)$$

where V_{T_i} and α_i denote the molar volume and the mean thermal expansion coefficient.

As mostly the partial quantities are not easily available for a salt composed of two ions the following approximation seems reasonable

$$\Delta V^* \cong \frac{1}{2} \frac{V_T \alpha T}{1 + \alpha T} \qquad (2)$$

where V_T and α mean here the molar volume and the mean thermal expansion coefficient for the salt.

Formula (2) has been applied to several solid and molten salts, giving mostly results not worse than 20% deviation from experimental values.

PB-22

KINETICS OF GAS-SOLID AND SOLID-SOLID REACTIONS IN ZIRCONIUM PHOSPHATE*

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Zirconium phosphate, $Zr(HPO_4)_2 \cdot H_2O$, is an ion exchanger with a layered structure.[1] In the anhydrous form it is capable of reaction with solid metal halides as in eq. (1).[2]

$$(1) \quad Zr(HPO_4)_2 + XMCl_n \rightleftharpoons ZrM_xH_{2-nx}(PO_4)_2 + nx\,HCl(g)$$

When M = Na^+, compounds are formed with x = 0.2, 0.8, 1 and 2. The reactions are diffusion controlled being slow for the forward direction and rapid in the reverse direction. For the reaction

$$(2) \quad Zr(NaPO_4)_2 + HCl \rightleftharpoons ZrNaH(PO_4)_2 + NaCl$$

the data could be represented by the equation

$$(3) \quad F = (1+\beta)[1 - \exp(T/\beta^2)\,\mathrm{erfc}(T/\beta^2)^{1/2}]$$

where F = fractional equilibrium attainment, $T = Dt/\ell^2$, ℓ = particle thickness, β = final fraction of exchange. Diffusion coefficients (D_t) range from 1.7×10^{-15} at 140°C to 2.7×10^{-14} cm²/sec at 222°C ($D_o = 2.6 \times 10^{-8}$) cm²/sec. Further reaction of $ZrNaH(PO_4)_2$ with HCl occurs at similarly fast rates.

The slowness of the forward reaction is attributed to Na^+ transport being restricted to move parallel to the layers. Thus, the surface area for the forward reaction is about $\frac{1}{100}$ that of reverse reaction as protons are not so restricted in their transport. A small sodium-sulfur battery was constructed using $Zr(NaPO_4)_2$ as membrane.

*Supported by Materials Science Division, National Science Foundation

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DETERMINATION OF DIFFUSION COEFFICIENT OF SOLID ELECTROLYTES FROM MEASUREMENTS ON POLARIZATION CELLS*

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A simple model is described for the study of polarization kinetics of cells of type Me/MeX/Blocking Electrode which can explain some of the experimental observations. The application of this model is demonstrated by measurements on a superionic material in the system $AgI-Ag_4P_2O_7$. The results indicate a lumped impedance behaviour due to diffusion process. The usefulness of this model is shown by effectively isolating the various contributions due to diffusion, double layer and electronic conductivity.

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PB-24

CHEMICAL DIFFUSION IN MULTICOMPONENT SOLIDS

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Fast ion transport in ionic solids is generally reflected by the corresponding high values of the appropriate diffusivities. The chemical diffusion coefficient, determined from interdiffusion, has been related to the tracer and intrinsic diffusion coefficients. In the past when considering such relationships, the assumption was made that the cross terms of the mobility tensor are negligible. In many cases, however, it is necessary to include these interactions which are reflected in the cross terms. By use of the interaction parameter the so-called thermodynamic factor can be well-characterized. In a like manner, a kinetic interaction factor is introduced to reflect the modification of kinetic parameters. The importance of these interactions has been demonstrated for many multicomponent systems of practical interest. By using the thermodynamic and kinetic interaction parameters, it is possible to mathematically relate the interatomic interaction of all the diffusing species to experimental values commonly measured.

INTERACTING BROWNIAN PARTICLES IN A PERIODIC MEDIUM

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In superionic conductors a situation can arise where the motion of ions cannot be described in terms of a discrete hopping process. For treating the low-frequency dynamics we employ a liquid-like model defined by a diffusion equation (Smoluchowski-equation) for many particles subject to pair forces and to a periodic single particle force due to the regular arrangement of counterions.

Various approximation schemes are used to study the dynamic structure factor and the frequency-dependent conductivity. First, we present a qualitative discussion based on a time-dependent mean-field approximation. We find that the conductivity depends sensitively on the interplay between the periodicity of the lattice and those wave vectors which characterize the short range order induced by the pair forces. Secondly, the results of the time dependent mean field approximation are tested against exact results for a one-dimensional hard-core model.[1] Thirdly, an approximate method[2] is used which relates the dc-conductivity to the spatial variation of the particle density. Numerical results are given for moderate densities and various forms of the pair potential.

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PB-26

STATICS AND LOCAL DYNAMICS OF SUPERIONIC CONDUCTORS NEAR THE PHASE TRANSITION

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The statics and dynamics of superionic conductors are investigated by means of a Hamiltonian, which takes into account the mutual interactions of the mobile ions and their interaction with the cage ions. The Hamiltonian is written as a function of the local density of the mobile ions on its available interstitial sites α in cell i, $N_{i\alpha}$, of the displacements of the cage ions $Q_{i\beta}$ as well as the corresponding momenta.

The time independent density-density and displacement-displacement correlation functions are calculated within MFA. It is shown that those correlations which are connected with the order parameter are divergent at the stability limits of the ordered and disordered phase and stay finite at T_c. When the mobile ions are coupled to acoustic phonons, the elastic constants show a softening at T_c when the coupling strength is large. When the coupling is weak no anomalous behaviour is observed.

The time dependent correlations have been calculated within Mori-theory, taking the local density $N_{i,\alpha}$ and the phonon coordinates of the cage as relevant variables. The T- and k-dependence of the dynamic correlation functions and especially the dispersion relations for the coupled modes are discussed. When the coupling is acoustic and the transition is of second order a Z-branch in the central peak dispersion near the critical temperature is found. In contrast, when the transition is of first order this Z-branch is hard to see. The frequency dependent conductivity is also discussed. It is pointed out that the local relaxation of the mobile ions between neighbored interstitial sites may cause the peak in the microwave region which has been measured by Funke et al.

PB-27

dup.

FREQUENCY DEPENDENCE OF HOPPING CONDUCTIVITY*

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We present calculation of the frequency dependence of hopping conductivity $\sigma(\omega)$ in two simple but non-trivial models. Although it has been recognized[1,2] that $\sigma(\omega)$ must increase with ω in a pure hopping model, we are aware of no previous explicit analytic results, although numerical computations have been performed on finite chains.[2] The first model (i) consists of two inequivalent sites A and B in an arbitrary two sublattice structure for which the particles are non-interacting except for hard core repulsions which prevent double site occupancy. The second (ii) is a one-dimensional (1D) lattice with equivalent sites in which there are nearest neighbor interactions as well as the double-site-occupancy exclusion. Results are valid for arbitrary particle density ρ in (i) but are restricted to low density in (ii) where we compute $\sigma(\omega)$ up to and including terms of the order of $\rho^3[\mathcal{O}(\rho^3)]$. In either model $\sigma(\omega)$ has the form $\sigma(\omega) = \sigma(\infty) - \dfrac{\sigma(\infty) - \sigma(0)}{1 + \omega^2\tau^2}$ with $\sigma(\infty) > \sigma(0)$, and explicit expressions are given for $\sigma(\infty)$, $\sigma(0)$ and the characteristic time τ. For equivalent sites in (i) or for $\mathcal{O}(\rho^2)$ in (ii) $\sigma(\omega)$ is independent of ω.

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*Work supported by the U. S. Dept. of Energy under Contract DE-AC04-76DP00789.

†A Department of Energy facility.

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PB-28

ORIGIN OF THE TWO-LEVEL SYSTEM IN SUPERIONIC CONDUCTORS

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The origin of the two-level (or multi-level) system, discovered by Anderson[1] to apply to superionic conductors as well as to glasses[2] at low temperatures, is discussed. Forward scattering, very low wavevector structure in the static VanHove correlation function, the structure factor S(k), for the system causes small, low wavevector roton-like minima with associated maxima in the collective boson (liquid phonon) dispersion relation[3], in addition to a more pronounced roton-like minimum at high wavevector. Each roton-like minimum and associated maximum will be a point on the liquid phonon dispersion relation where the liquid phonon group velocity goes to zero. As such, each will produce a peak in the density of states in energy. These peaks, at least from the low wavevector structure in S(k),will be at low frequency and have a low frequency difference. The peak originating from the high wavevector regime in S(k) associated in a crystal with the Brillouin zone boundary, iff wavevector is a well defined quantum number in that regime, will fall at whatever frequency the roton-like minimum in the dispersion relation appears at. This latter roton-like minimum, with its associated density of states peak, will be severly broadened via liquid phonon anharmonicity and can only constitute one level, however, the broadening could make it appear as a group of levels. Application to alkali-β-alumina superionic conductors will be made.

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EFFECTS OF ABSORBED WATER ON NMR LINESHAPE AND T_1 IN Na β"-ALUMINA*

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We have performed NMR observations of both lineshape and spin lattice relaxation time T_1 at 24 MHz of Na in Na β"-alumina powder containing different amounts of water. For samples exposed to 100% humidity, our measurements indicate that water rapidly penetrates the conduction plane on a microscopic scale. We observed that absorbed water results in a greatly reduced linewidth and correspondingly reduced quadrupolar interaction at each ^{23}Na nucleus. Furthermore, the presence of water changes the Na spin lattice relaxation time. Exposure to moisture changes the nature of the lineshape from that due to a second order quadrupolar broadened powder to that due to a simple dipolar broadened system. Partial drying of the powder at higher temperatures restores the original quadrupolar broadened line structure. Even for partially dried samples exhibiting the original fully quadrupolar-broadened lineshape, our T_1 measurements still showed effects from the small amounts of remaining water. In particular, the temperature dependence of T_1 of powder dried at 250°C yields a lower activation energy for motion and a broader T_1 minimum than for a dry sample.

Immersion of powdered Na β"-alumina in water strongly effects the Na NMR lineshape within minutes. The immersion process also leaches out some of the sodium. Water completely penetrates bulk sintered samples as well, but requires weeks to do so in these samples, instead of the minutes required in powders.

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Al^{27} NMR IN SINGLE CRYSTALS OF β-ALUMINAS*

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The first- and second-order quadrupolar shifts of Al^{27} in single crystals of M-β- aluminas (M = Li, Na, K, Ag, Tl and NH_4) have been studied as a function of crystal orientation in the magnetic field. The various spectral lines have been assigned to different crystallographic aluminum positions. The Al^{27} spectrum is scarcely affected by changes in temperature and cationic substitution. Instead, its saturation behavior is drastically altered by both factors. This indicates that the spin-lattice relaxation rates of Al^{27} are strongly affected by the motion of ions in the mirror plane. As a function of temperature, the Al^{27} relaxation rates go through a maximum, the position of which can be related to the mobility of ions in the mirror plane.

The reasons why Al^{27} relaxation rates are a rich and reliable source of information for ion motion in the plane will be discussed.

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EVALUATION OF CATION DISTRIBUTION IN Li/Na β-ALUMINA FROM FIRST-ORDER QUADRUPOLAR NMR SPECTRA

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In an earlier ^{7}Li NMR study of lithium-exchanged Na-β-alumina[1] we observed and reported first-order quadrupole effects on room temperature lithium spectra. These data indicated an averaged electric field gradient which was strongly dependent on exchange concentration with values of e^2qQ/h ranging up to 17.0 kHz for a 91 mole % lithium-exchanged sample. This paper reports results of low- and intermediate-temperature measurements of the quadrupole interactions in single crystals of lithium-exchanged sodium β-alumina. Interpretation of the low temperature data (~85 K) indicates that the lithium motion is effectively frozen out and the presence of three independent EFG tensors can be identified. These tensors are independent of lithium exchange, and they have been correlated with theoretical tensors calculated for various sites in β-alumina, based on a simple point-charge model. Samples with different exchange concentrations differ in their relative population of sites inferred from the observed intensities of lines forming the EFG rotation patterns. In addition, intermediate temperature data is allowing detailed characterization of the lithium motion among these sites.

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PB-32

ac CONDUCTIVITY AND NMR RELAXATIONS IN IONIC CONDUCTORS

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The ac conductivity of Na β-alumina has been studied recently by several groups. The combined frequency and temperature dependences of the ac conductivity σ have not yet been understood adequately. Qualitatively, at the lowest frequencies ω, $\sigma(\omega) \sim \omega^n$, the exponent n is close to unity at cryogenic temperatures but its value decreases and approaches zero as the temperature is raised towards room temperature.

We shall point out that these anomalous behaviors stated here are not unique to Na β-alumina, but prevalent in almost any dielectrics that have hopping charges whether electrons or ions. Examples will be given. We have recently advanced a general theoretical model[1,2] that explores the origin of the universal dielectric response of condensed matter. This model will be specialized to the ionic conductors to explain the anomalous combined frequency and temperature dependences of $\sigma(\omega)$. The physical origin of these dependences is traced to the existence of a class of correlated state excitations in ionic conductors. Most recent data on Hollandite will also be presented and discussed in conjunction with that of Na β-alumina.

On the same physical basis we have extended our theory to account for NMR spin-lattice relaxations in ionic conductors. The frequency and temperature dependences of T_1, the spin-lattice relaxation time, are calculated. The discrepancy of the attempt frequency determined from NMR relaxation measurements with that determined by other methods can be explained in our model calculations. Comparisons of theory with experiment are made for Na β-alumina.

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PROTON MAGNETIC RESONANCE IN NH_4-β AND NH_4-β" ALUMINA

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H^1 NMR studies of NH_4-β and NH_4-β" single crystals and NH_4-β polycrystalline samples are being made from room temperature to LNT. Wide line NMR data characterize the second moment dependence on crystal orientation and temperature. In NH_4-β, two spectral lines have been indentified. A broad line originates from a reorientation motion of protons in the NH_4^+ ion. A narrow line, present above -30°C may be a precursor to the motion associated with NH_3 loss from the sample which occurs at 350°C. Pulsed NMR methods to delineate T_1 dependence on crystal orientation and temperature are in progress. The paper will review preparation, composition, and thermal stability data on these materials.

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PB-34

CONDUCTIVITY MECHANISMS IN THE SUPERIONIC PHASES OF AgI AND Ag_2S AS DETERMINED BY NEUTRON DIFFRACTION

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Careful neutron diffraction measurements on single crystals of the silver conducting BCC phases of AgI and Ag_2S were performed at temperatures between 160 and 325 °C. They show that although the anion frameworks are the same, the distribution of the mobile silver ions differ markedly, due to different cation concentrations and cation-anion bonding characteristics. In αAgI the observed silver probability density duplicates precisely the reported activation energy of .06 eV at the saddle point between nearest neighbor tetrahedral sites: indicating that nearest-neighbor jumping of independent atoms, with a distance of about 1.78A, is the basic step in the diffusion process. In Ag_2S the observed silver probability density is much more diffuse, even though the reported activation energy for diffusion is approximately a factor of 2 larger than that for αAgI. This is interpreted in terms of significant positional disorder of the silver ions, and significant silver-silver interaction, favoring a "caterpillar" type mechanism for silver ion motion.

NMR AND NEUTRON DIFFRACTION STUDIES OF MIXED CONDUCTORS Li_x MPX_3

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Earlier NMR measurements on the mixed conductors Li_xNiPS_3 (1) (prepared by the n-buthyllithium technique) indicated a very low mobility of lithium atoms at thermodynamic equilibrium ($D \simeq 10^{-13}$ cm^2 s^{-1}), in contrast with the good electrochemical activity of these compounds (2). At the same time, the study of change in electronic and magnetic properties of the host as a function of intercalation rate revealed the appearance of a new phase for x values larger than 0.5.

Similar experiments performed on electrochemically intercalated compounds demonstrate the same behaviour as far as lithium mobility and the change in magnetic properties are concerned. The nature of the second phase ($x > 0.5$) and the lithium sites occupancy ($x < 0.5$) will be discussed in light of new NMR and neutron diffraction results. NMR measurements have also been extended to similar compounds Li_xMPX_3 (M = Ni, Fe, Mn, X = S, Se) and reveal a very different behaviour of sulfur and selenium compounds.

+Laboratoires associés au C.N.R.S.

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PB-36

ANION DISORDER IN TWO FLUORITES AT HIGH TEMPERATURES AS DETERMINED BY NEUTRON DIFFRACTION

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The fluorite structure compounds strontium chloride, $SrCl_2$, and lead fluoride, PbF_2, exhibit diffuse transitions at temperatures T_c, ~1000K and ~700K respectively, above which the conductivity increases to a value almost that of the molten salt. The high conductivity is due to the mobility of the anions and above T_c there exists a correspondingly high degree of disorder in the anion sublattice. The conduction mechanism which has usually been postulated at low temperatures involves Frenkel defects in which an anion is displaced to populate the normally vacant cube-centre interstitial site, but the relevance of this site at high temperatures when the defect concentrations are high has been questioned as a result of recent model calculations(1)(2). In order to study the time-averaged structure of the disordered anions, powder and single crystal neutron diffraction experiments have been carried out on these two compounds at temperatures up to T_c and above. The powder and single crystal data for $SrCl_2$ give very similar results. In PbF_2 the powder data proved to be unreliable due to sintering of the sample; however, the single crystal measurements were successful. For both compounds the data show a dramatic increase in the anion Debye-Waller factor and in the effects of anharmonicity in the region of T_c. Analysis of the data on $SrCl_2$ indicates that only a small proportion of anions, ~3.5%, leave each regular site in the high temperature disordered phase. In PbF_2, however, this figure is found to be much larger, ~21%. The preferred location of these displaced anions will be discussed.

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INVESTIGATION OF ANION MOTION IN FLUORITES AT HIGH TEMPERATURES USING NEUTRON QUASIELASTIC SCATTERING

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Strontium chloride, $SrCl_2$, and calcium fluoride, CaF_2, each exhibit a diffuse transition to a state of high ionic conductivity at a temperature T_c, ~1000K and ~1430K respectively, arising from a dynamic disorder in the anion sublattice. In order to obtain information on the anion diffusion at elevated temperatures we have carried out low energy transfer (quasielastic) neutron scattering experiments on single crystal samples of $SrCl_2$ and CaF_2. The measurements were made using high resolution (~0.1 meV) triple-axis spectrometers. The quasielastic scattering is observed to develop about 100°C below T_c, and as the temperature is raised through T_c and above, the integrated intensity increases in parallel with the degree of disorder in the system estimated from the disorder heat content. At elevated temperatures, the areas of reciprocal space where strong quasielastic scattering is observed fall on a shell of radius ~$2\mathring{A}^{-1}$ with maximum intensity in certain regions, for example around the (2.3,0,0) and (1,2,2) points. The strong wavevector dependence of the intensity suggests that the scattering is coherent in nature, and this has been confirmed by isotopic substitution experiments on $SrCl_2$ and by the fact that the scattering from CaF_2 is intrinsically coherent. The Lorentzian energy widths above T_c, typically 0.5 meV in $SrCl_2$ and 3.0 meV in CaF_2 (FWHM) are of the same order as estimated from the diffusion constants; however, the variation with temperature is much weaker than expected. Qualitative interpretation of our results suggests a model of a dense anisotropic liquid for the mobile ions.

PB-38

NEUTRON DIFFRACTION STUDY OF Cu_6PS_5Br AT 293 K AND 473 K

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There are two different ways of describing the crystal structure i.e. the scattering density distribution of fast Ag^+- and Cu^+-conductors. One treats the thermal motions of the ions in a harmonic approximation; this treatment necessitates a splitting of the occupancies in two or more locations. The other, significantly better way is the anharmonic treatment, as shown by Cava et al.[1] for α-AgI and as will be shown for α-Cu_6PS_5Br.

Cu_6PS_5Br belongs to a new family of structure: the "argyrodites". Various ordered structures of low symmetry occur; at higher temperatures the argyrodites become cubic with disordered cation-sublattices. Cu_6PS_5Br crystallizes at room-temperature in the disordered phase (T_c: 268 K) and shows a distinct Cu^+-conduction (σ_{ion}: $1.5 \cdot 10^{-5}$ $(\Omega cm)^{-1}$ at 293 K, $1.2 \cdot 10^{-3}$ $(\Omega cm)^{-1}$ at 473 K).

Neutron diffraction measurements were conducted at 293 K and 473 K. Least-squares refinements were carried out, using the program of Finger & Prince[2], which allows the refinement of third and fourth order thermal tensors. The calculations show, that the Cu-density distribution must be described, using the harmonic approximation, by at least two Cu-positions. In the anharmonic treatment this distribution is completely accounted for by higher order thermal tensors of only one Cu-position; they indicate a severely anharmonic motion of the Cu^+. Particularly remarkable are the large harmonic and anharmonic thermal parameters of the anions; they indicate an important contribution of the anion-motions to the cation-conduction.

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PB-39

SINGLE PARTICLE EXCITATIONS IN $RbAg_4I_5$

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In an inelastic neutron experiment on $RbAg_4I_5$ a broad quasielastic peak was observed throughout Q-space.[1] As the temperature was lowered the quasielastic peak became a broad propagating excitation with $\hbar\omega \sim 2.2$ meV.[1] This excitation was measured along several symmetry directions and it exhibited little dispersion. This confirms that the original idea of a single particle excitation corresponding to the Ag^+ ions moving within a potential well created by the rest of the lattice. The temperature dependence of this excitation is consistent with the calculations of Geisel where the line width is determined by the interaction of the mobile ions with the other phonons of the lattice.[2]

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† Supported in part by NSF Grant No. DMR 77-23999.

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ABSTRACTS

of

CONTRIBUTED PAPERS

Poster Session PC

NMR AND CONDUCTIVITY STUDIES OF IONIC TRANSPORT IN LaF_3

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We have shown that a powerful tool in the identification of diffusion mechanisms in ionic crystals is the combination of nuclear magnetic resonance (N.M.R.) and electrical conductivity techniques.

In recent work we have used this method to study alkali halides[1] and alkaline fluorides[2]. A particularly interesting application of this approach was shown in our study of the "superionic" region of PbF_2[3,4].

The present paper reports the extension of our work to the study of LaF_3. LaF_3 has a relatively complicated crystal structure which makes a detailed analysis of the transport properties somewhat difficult. We have measured the ^{19}F N.M.R. relaxation times T_1, T_2, $T_{1\rho}$ over a wide temperature range in single crystals of LaF_3. Parallel conductivity studies of these same crystals have also been made.

The conductivity results appear relatively simple in that they break down into identifiable intrinsic and extrinsic regions. A strong anisotropy has been observed. Also, large polarization effects have been found which possibily originate from a surface oxide layer. The N.M.R. relaxation times show a complicated dependence on temperature. This has been analysed in terms of two types of fluoride ion motion.

A comprehensive analysis of the results will be reported.

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PC-2

THE ANIONIC CONDUCTOR $PbSnF_4$: STUDY OF THIN FILMS AND CERAMICS

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Preliminary studies have shown that binary fluorides such as PbF_2 and SnF_2 have relatively high ionic conductivities, attributed to the presence of cations having a strong polarisability. Consequently a high mobility of the F^- ion was expected for $PbSnF_4$. Samples made of sintered powder show three allotropic varieties with reversible transitions. The low temperature form (α) is orthorhombic and gives at 20°C a conductivity of $9\ 10^{-4}\ \Omega^{-1}\ cm^{-1}$, with an activation energy E = 0.42 eV. The second form (tetragonal), gives at 20°C, after quenching, a conductivity of $1.2\ 10^{-3}\ \Omega^{-1}\ cm^{-1}$ with E = 0.20 eV. Thin films have been obtained by thermal evaporation. A quantitative analysis performed by X-ray fluorescence measurements shows the strong dependence of the film composition with the evaporation rate. Stœchiometric $PbSnF_4$ has been obtained with rates greater than 3000 Å/mn. The structure of the films is always cubic, and corresponds to the highest temperature variety (γ). The optical gap is estimated, from absorption measurements, to be about 3 eV. The conductivity is $1\ 10^{-3}\ \Omega^{-1}\ cm^{-1}$ with E = 0.30 eV. In both forms, sintered samples and thin films, a treatment of the impedance and admittance plots have been performed. The temperature and frequency behaviour of the interface capacitance was determined.

PC-3

ACTIVATION VOLUMES OF SUPERIONIC CONDUCTORS WITH THE FLUORITE STRUCTURE*

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Activation volumes of several crystals with the fluorite structure and some related materials have been obtained from the pressure dependence of the ionic conductivity. The data are taken under hydrostatic conditions with argon gas pressures up to 0.6GPa (6 kbars) and for temperatures up to 1200°C. The activation volumes are found to be small and positive and are consistent with a Frenkel defect model of the conductivity. The materials examined irclude: SrF_2, BaF_2, CdF_2, PbF_2, $SrCl_2$, $PbCl_2$ and MgF_2.

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PC-4

ULTRASONICS IN IONIC CONDUCTING FLUORIDE FLUORITES

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Measurements of the ultrasonic velocity in cadmium fluoride are reported from room temperature to temperatures near the Faraday transition from insulator to solid electrolyte. This work is compared to Brilliouin scattering studies[1] on other fluorides of the fluorite structure in an attempt to provide empirical information on this simple class of high temperature solid electrolytes. The CdF_2 appears to have a transition from insulator to solid electrolyte near 800 K.

[1] C. R. A. Catlow, J. D. Comins, F. A. Germano, R. T. Harley and W. Hayes, J. Phys C 11, 3197 (1978).

AMMONIUM IONS ARE "ROLLING" IN β ALUMINA

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The motion of NH_4^+ ions in non-stoechiometric β alumina single crystals has been observed at liquid helium temperatures and between 77°K and 360°K, and the effects on the proton NMR lineshape are reported. We show that at helium temperatures the ions in BR positions exhibit rapid quantum tunnelling and have a C_2 axis parallel to the $\vec{c}$ axis of the crystal. On the contrary, the ions in mO positions are motionless. The spin isomerism theory allows a quantitative interpretation of the spectra.

Between 77°K and 240°K there is a single line corresponding to rapid 90° reorientation around a C_2 axis perpendicular to $\vec{c}$. Above 240°K jump diffusion begins to occur and there is a corresponding line narrowing. The activation energies found from NMR and conductivity are the same showing that the elementary motion of the ion is a translation plus rotation jump : ammonium ions are "rolling". Good agreement is found between electrical conductivity and NMR data showing agreement also for the prefactors.

PC-6

ORDER-DISORDER TRANSITION BETWEEN OFF-CENTER POSITIONS IN THE MIXED CONDUCTOR Cu_3VS_4

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Cu_3VS_4 exhibits a tridimensional network of crystallographic channels through which a few interstitial Cu^+ move with high mobility at room temperature. X-Ray studies have shown that each copper atom of the host lattice is located in one of four equivalent off-centered positions (o.c.p.).[1]

We think that the situation where one conducting ion is surrounded by a "deformable" environment due to the existence of several o.c.p. for the neighbors is favorable to high mobilities (A number of superionic conductors exhibits such a situation). Here we are interested in the low temperature behavior (static + dynamic) of the interacting system formed by the off-centered atoms.

We report nuclear relaxation of ^{63}Cu, ^{65}Cu and ^{51}V which is ultrafast : $T_1 \sim 1$ sec for ^{63}Cu and ^{65}Cu and 10 sec for ^{51}V at 1.5°K. Moreover the observation of a sharp singularity in the variation of T_1 (^{51}V) at 9°K indicates an order-disorder transition in the o.c.p. occupancy.

We develop a theoretical model based on four equivalent wells for each copper atom. The transition temperature is in accordance with an electric dipole-dipole interaction between the o.c.p. It is the excitation of pseudo-spin waves due to tunnelling which is responsible for ultrafast nuclear relaxation. We solved an Ising like model for the fundamental state which is shown to have a 2 × 2 × 2 basic lattice cell.

[1] N. LeNagard, G. Collin, O. Gorochov, H. Arribart, A. Willig, B. Sapoval in Superionic Conductors, edited by G.D. Mahan and W.L. Roth, Plenum Press, New York (1976).

CHEMICAL ORIGIN OF THE MOBILE IONS AND NUCLEAR RELAXATION IN Cu_3VS_4

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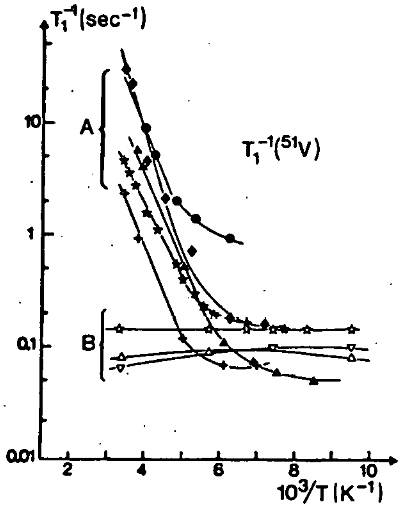
Nuclear spin lattice relaxation of ^{51}V has been studied in the range 100-300°K in the mixed conductor Cu_3VS_4. This material exhibits a small ionic conductivity due to highly mobile interstitial Cu^+ ions.[1] The experiments show that there exist two classes of samples (denoted by A and B in the figure). In samples A the relaxation at room temperature is fast ($T_1 \sim 0.1$ sec) and varies exponentially with 1/T. This relaxation is due to the motion of interstitials Cu^+ which modulates the quadrupolar interaction seen by the ^{51}V nuclei. The activation energy is 0.15 eV and the relaxation rate is directly proportional to the concentration of mobile ions. In samples B the relaxation is slow ($T_1 \sim 10$ sec) and almost independent of temperature. The concentration of conducting ions is very small and the relaxation is due to paramagnetic impurities.



The chemical difference between A and B samples holds in the fact that samples A contain chlorine as impurities (samples A are grown by Cl_2 vapor transport) and not samples B. This proves that the existence of an ionic conductivity in Cu_3VS_4 is related to the presence of chlorine, the extra-electrical charge of a mobile interstitial Cu^+ being compensated by a fixed Cl^- interstitial.

1. H. Arribart, B. Sapoval, O. Gorochov, N. LeNagard, Solid State Commun. 26, 435 (1978).

PC-8

PRESSURE DEPENDENCES OF THE ELASTIC CONSTANTS OF CUBIC PbF_2 AT 296 K AND TEMPERATURE DEPENDENCES OF THE SPECIFIC HEAT OF CUBIC AND ORTHORHOMBIC PbF_2*

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We have measured the effect of hydrostatic pressures up to 3 kbar on the velocity of longitudinal and shear ultrasonic waves in cubic PbF_2 at 296 K and the specific heat of both cubic and orthorhombic PbF_2 up to temperatures above where the superionic transition occurs in cubic PbF_2 (between 650 K and 750 K).

The pressure dependences of the elastic constants of cubic PbF_2 determined from our velocity data indicate no mode softening with increasing pressure even though a transition to the orthorhombic phase is known to occur near 4 kbar. These results are discussed in terms of the Demarest et al. modification of the Born criteria for lattice stability, a soft transverse acoustic mode near the zone boundary, and the Axe-Srinivasan shell model.

The heat capacity of the cubic form exhibits a maximum which is discussed in terms of the superionic transition.

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MAGNETIC TAGGING OF ION DIFFUSION IN PbF_2*

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We report on a F^{19} NMR study of PbF_2 which was substitutionally doped with Mn^{2+} in concentrations (c) ranging from 1 percent Mn to nominally pure PbF_2. Both linewidth (ΔH) and pulsed (T_1^{-1} and T_2^{-1}) measurements were made in the temperature (T) region 25° to 750°C, at frequencies extending from 16 to 90 MHz. The presence of paramagnetic impurities drastically alters the relaxation rates T_1^{-1} and T_2^{-1} in proportion to c once ion diffusion becomes more important than nuclear spin diffusion. The motional narrowing of the nuclear dipole-dipole interaction is followed first, by an increase and then by a decrease of ΔH with increasing T. The maximum in ΔH occurs at $T \approx 500°C$ and was shown(1) to result when the F^- ion hopping rate $\omega_h \simeq \omega_{HF}$, the F^{19} transferred hyperfine interaction with a neighboring Mn^{2+} ion. Significant deviations from our model theory(1) and that of Richards(2) are found when $\omega_h >> \omega_{HF}$. The T_1^{-1} measurements exhibit an initial peak as T increases, which we associate with the electronic dipolar (I^+S^z) interaction, and approaches a second one at higher T which results from the transferred hyperfine (I^+S^-) coupling. The lack of frequency dependence to $1/T_1$ on the low temperature side of the initial peak is not in accord with Richards(2) theory.

(1) R. D. Hogg, S. P. Vernon, V. Jaccarino, Phys. Rev. Letters 39, 481 (1977).

(2) P. M. Richards, Phys. Rev. B 18, 6358 (1978).

* Research sponsored by DOE Project Number EY76-S-03-0035 PA244

PC-10

LATTICE DYNAMICS OF BINARY SUPERIONIC CONDUCTORS

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The experimentally observed Raman results in the superionic phases of AgI and CuI are very broad with no sharp features. Quite a few theoretical papers, based on single particle models, have been published attempting to explain these and related infrared results. However, when the experimental Raman results are plotted in reduced form[1], distinct features in the vicinity of the TO and TA phonon branches of the room temperature crystal structures are apparent. We have theoretically calculated the spectral results (for AgI and the Cu halides) using standard lattice dynamic methods *but* properly taking the disorder into account.[2] The results are encouraging for AgI and CuI where an experimental comparison can be made and point out that many of the properties of simple superionic conductors can be understood in terms of standard harmonic lattice dynamics but with disorder taken into account.

1. G. Burns, F. H. Dacol and M. W. Shafer, Phys. Rev. B*16*, 1416 (1977), and Solid State Comm. *19*, 291 (1976).
2. R. Alben and G. Burns, Phys. Rev. B*16*, 3746 (1977).

Motion of Charge Carrying Ions in Sodium β-Alumina.*

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Abstract:

We report the results of a molecular dynamics simulation of the motion of charge carrying ions in sodium β-alumina. Exact account is taken of the forces on the ions in the conduction plane but the ions in the spinelblocks are treated approximately. The computed values of the coefficients of selfdiffusion are in good agreement with those observed experimentally. Density maps show that in stoichiometric β-alumina the sodium ions occupy positions around the Beevers-Ross and mid-oxygen sites. When extra sodium ions are added to the lattice the anti-Beevers-Ross sites are occupied as well. The diffusive motion of the charge carrying ions is analysed to ascertain whether diffusion proceeds continuously or by a jump mechanism.

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PC-12

FAST ION TRANSPORT IN $Sr\,C\ell_2$

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A molecular dynamics study of $SrC\ell_2$ has been carried out over a range of temperatures at constant volume. We find qualitative agreement with experiment for both the magnitude and the temperature dependence of the electrical conductivity. We present contour maps of the mean ion densities; these bring out the following points: (1) on average the anions are localised about their regular sites; (2) there is no accumulation of density at the cube-centre sites even at the highest temperature; (3) increase of temperature causes an increase of density along the line joining nearest neighbour regular anion sites. We find that the diffusive motion can be analysed in terms of discrete hops with a large ratio of residence to hopping times.

The hopping of anions can be approximately described in terms of the motion of vacancy and interstitial defects. The concentration of defects so obtained is only a few percent even at the highest temperature. We present typical hopping trajectories which show that hopping anions generally travel rapidly and directly between lattice sites. The strong correlation between hopping is demonstrated by means of a hopping catalogue.

ION FLOW IN A SUPERIONIC CONDUCTOR

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An excluded volume model has been proposed[1] to explain the unusual cation-anion pair correlations which have been observed in superionic conductors[2]. It is assumed that the positions of the conducting ions within the crystalline lattice are determined predominantly by the short-range cation-anion core-core repulsion, modeled as a softened "hard sphere" interaction. The excluded volume model yields a distribution of mobile ions which is uniform except for their being excluded from spheres centered at the positions of the immobile ions, as determined from diffraction studies. The resulting cation-anion pair correlation functions have been shown to be in excellent *quantitative* agreement with the pair distribution functions derived from EXAFS measurements on AgI and on the Cu halides, in both the normal and superionic phases[3].

From these measurements, we have deduced the three-dimensional potential, V(r), seen by the conducting ions in the crystal. On the further assumption that the conducting ions have energy and velocity distributions like that of charged ions in a dilute Boltzmann gas, we have calculated the probability that an ion will hop from one lowest energy site to another in the crystalline lattice. This leads to an estimate of the temperature-dependent ionic conductivity which correlates strongly with experimental determinations in these materials. By explaining many features of the observed conductivity in both the normal and superionic phases, this model supports the view that the conduction processes in these two phases are qualitatively identica.

[1] T. M. Hayes, J. B. Boyce and J. L. Beeby, J. Phys. C11, 2931 (1978).

[2] See, for example, J. B. Boyce, T. M. Hayes, W. Stutius and J. C. Mikkelsen, Jr., Phys. Rev. Lett. 38, 1362 (1977).

[3] J. B. Boyce and T. M. Hayes, "Structure and Its Influence on Superionic Conduction: EXAFS Studies" in *Physics of Superionic Conductors*, ed. by M. B. Salamon (Springer-Verlag, New York, 1979), Chap. 2.

PC-14

STRUCTURAL AND DYNAMICAL BEHAVIOR OF α-AgI

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Molecular-dynamics calculations can provide valuable information about the microscopic mechanism in superionic conductors. The silver subsystem of α-AgI is disordered and shows strongly anharmonic behavior. By means of molecular-dynamics calculations it is possible to treat anharmonicities without approximations.

In two previous papers /1,2/ a molecular-dynamics model (vibrating-ion model) was proposed for the description of correlations in space and time in α-AgI. In this paper a modified version of this model is proposed in order to obtain more realistic results for the correlation functions. The points investigated are: (i) the single-particle motion, (ii) the collective behavior of the system, (iii) the coupling of single and collective modes.

Comparison is made with computer experiments on α-AgI performed by Vashishta and Rahman /3/.

/1/ W. Schommers, Phys. Rev. Letters <u>33</u>, 1536(1977)
/2/ W. Schommers, Phys. Rev. B <u>17</u>, 2057(1978)
/3/ P. Vashishta and A. Rahman, Phys. Rev. Letters <u>40</u>, 1337(10978)

IONIC TRANSPORT IN SILVER HALIDES

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Of the conventional ionic conductors the silver halides AgCl and AgBr have the highest conductivity while in several fast-ion conductors it is the silver ion which is the mobile species. For these reasons a re-examination of ionic transport in AgCl and AgBr seemed timely. The ionic conductivity of these two materials has been measured recently by Friauf and co-workers. If these data are interpreted in terms of the conventional Frenkel defect model with temperature-independent defect enthalpies and entropies, then at high temperatures the conductivity calculated from defect parameters fitted at intermediate temperatures, lies below the experimental values. Friauf concluded that g_F, the Gibbs free energy of Frenkel defect formation, must decrease faster with temperature than is predicted by the usual thermodynamic relation h_F-Ts_F, and ascribed this in very general terms to a loosening of the lattice.

Using the (by now) well-tried methods of calculating defect energies that have been developed by Norgett we have calculated the defect formation and migration energies for AgCl and AgBr using a quasiharmonic model which allows for the thermal expansion of the crystal. The Frenkel defect formation energies are of a similar magnitude to the experimentally determined values and, not surprisingly, decrease with increasing temperature. We have also shown that ion deformation is an essential feature of silver-ion transport. Theoretical calculations of migration energies that allow for ion-deformation in the saddle-point configuration yield results that are in excellent agreement with experimental values.

PC-16

THERMOPOWER MEASUREMENTS IN $RbAg_4I_5$ FILMS

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The thermopower of fast ionic conductors is generally predicted to have the form:

$$S(T) = Q^*/qT + H$$

where Q^* is the heat of transport, q is the charge of the carrier and H is a collection of entropy terms. Published data on pressed pellet samples and on solid samples obtained by freezing molten $RbAg_4I_5$ show limited agreement with one another. Striking disagreements occur in the temperature dependence of the raw data while contradictory assumptions about H are used in fitting the data to the predicted form.

We have used a differential method to measure S in evaporated $RbAg_4I_5$ films between 200 and 350K. Our raw data are generally consistent with the predicted temperature dependence and with some of the pressed pellet data. Q^* is comparable to the activation enthalpies reported from conductivity studies but H is lower than the values obtained in previous thermopower studies. S at room temperature is approximately 0.4 mV/K. The effect of the experimental configuration on H will be discussed.

VISUAL OBSERVATION OF THE TRANSPORT OF SILVER THROUGH A $RbAg_4I_5$ FILM

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We have observed and filmed, by time lapse photography, the transport of silver laterally across a thin (~1 μm) film of $RbAg_4I_5$. The dynamics of the ion motion, the various paths which the ions take in building up metallic filaments and the depletion of silver from the anode are made strikingly visible and will be discussed.

PC-18

GROWTH OF α-Ag_2S AND α-Ag_2Se SINGLE CRYSTALS THROUGH A CAPILLARY TUBE

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Cylindarical single crystals were grown by rotation of the ampoule in which seed was selected spontaneously through an inner capillary tube as shown in Fig.1. Solid-state transport of Ag atoms, which was achieved by the ambipolar diffusion, and vapour transport of S_2 or Se_2 were used for the growth reaction. This technique is only applicable to mixed conductors of electrons and ions.

Facet of {110} was appeared at the growing front of the crystal below about 480°C which was the surface roughening temperature. The observed growth direction, which was measured by the facet angle, was scattered around <111> orientation from about 10°to 30°. One is able to say that there is not a prefered orientation in this technique with spontaneous nucleation.

The crystals were converted to the low temperature phase at room temperature. They were reconverted to the single crystals of the high temperature α phase. It was confirmed by both the Laue X ray method and the regrowth experiments in which a new single crystal grew successively from a reconverted single crystal.

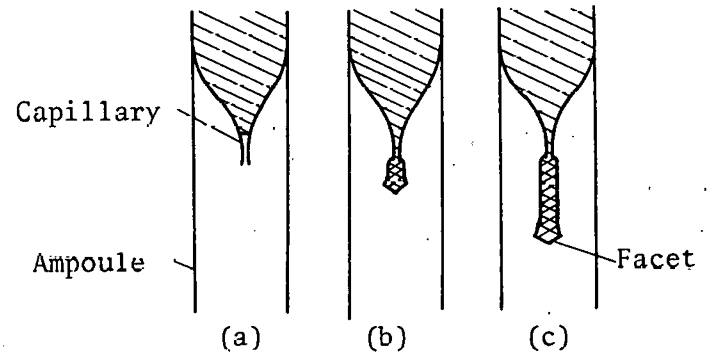

Fig.1 Schematic drawing of the growth process.

T.Ohachi and I.Taniguchi, J. Crystal Growth 40 (1977) 109.
T.Ohachi and B.R.Pamplin, J. Crystal Growth 42 (1977) 592.

THERMOELECTRIC POWER STUDIES OF PHASE TRANSITIONS IN FAST ION CONDUCTORS*

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In studying the thermoelectric power (TEP) of the fast ion conductors α-AgI and Pyridinium silver iodide ($PyAg_5I_6$) features were seen that do not appear in the low frequency conductivity. Since the TEP is a zero current measurement, it does not suffer from contact and carrier equilibrium problems. Use of small temperature gradients (0.1 to 0.5°K), and computer assisted data gathering and analysis allowed us to collect a large amount of data near the first and second order phase transitions in these materials.

In both types of phase transition a large sharp decrease in the thermoelectric power is seen immediately following the transition to the higher conductivity state. The broad transition seen in the specific heat and low frequency conductivity of $PyAg_5I_6$[1] is noted by a change of slope of the TEP, similar to that seen in the conductivity measurement. Supercooling of α-AgI by as much as 10°K is also seen.

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*Supported in part by the Research Corporation, and the Petroleum Research Fund administered by the American Chemical Society.

[1] T. Hibma, Phys. Rev. B15, 5797 (1977).

PC-20

STATIC AND DYNAMIC NMR EFFECTS AROUND THE 209 K PHASE TRANSITION IN $RbAg_4I_5$.

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We have extended our previous NMR investigations of $RbAg_4I_5$ powder samples[1] to single crystal specimens. We report first results obtained in the superionic phases between 160 and 300 K.

From the orientational dependence of the quadrupole splitting of the ^{87}Rb resonance the presence of 4 equivalent Rb sites in the α phase has been deduced. The electric field gradient tensors at the Rb sites are axially symmetric in accord with crystallographic data[2] and thus correcting our previous conclusions drawn from less reliable powder data. However, it has been confirmed that the 209 K transition is of first rather than second order[1].

The spin-lattice relaxation time, T_1, has been measured through the 209 K phase transition. Between 160 and 300 K $1/T_1$ is proportional to exp(0.11 eV/kT) except near the transition where $1/T_1$ exhibits a well pronounced peak. The relaxation is discussed in terms of Ag diffusion including critical fluctuations at the transition temperature.

1. D.Brinkmann, W.Freudenreich, H.Arend, J.Roos, Solid State Commun. 27, 133 (1978)
2. S.Geller, Solid Electrolytes, Topics in Applied Physics, Vol. 21, Springer (1977).

DIFFUSION PROCESSES IN Li_3N STUDIED BY ^6Li NMR

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We have performed ^6Li NMR measurements in Li_3N single crystals in order to check conclusions drawn from a recent ^7Li NMR study[1] concerning diffusion processes and the mechanism of NMR relaxation.

The variation of the quadrupole splitting of the ^6Li resonance with temperature supports our previous conclusions[1]. Below about 350 K diffusion of the Li ions is mainly restricted to the Li_2N layer. At progressively higher temperatures a second process becomes marked: an exchange of Li ions between Li- and Li_2N-layers. Eventually the intra- and the inter-layer diffusion as a whole attain a liquid-like behaviour.

Below about 300 K the spin-lattice relaxation of ^6Li is dominated by interaction with paramagnetic impurities (with relaxation times T_1 of the order of 10 s). The mobile ^6Li ions can migrate to the vicinity of these impurities where they are relaxed by dipolar magnetic interaction. However, for ^7Li the dipolar relaxation is only about 10 % of the total relaxation which is dominated by quadrupolar interactions. These differences in the relaxation mechanisms show up in different dependences of the relaxation time on crystal orientation thus exhibiting the two-dimensional character of the intra-layer diffusion.

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[1] D.Brinkmann, W.Freudenreich, J.Roos, Solid State Commun. 28,233 (1978)

PC-22

FAST IONIC CONDUCTION IN SOLID LITHIUM NITRIDE HALIDES

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The electrical conductivities of several lithium nitride halides have been investigated. The compounds belong to the quasi binary system Li_3N - LiX (X = Cl,Br,I) and have been prepared by annealing mixed powders of lithium nitride and halide. All materials are predominantly ionic conductors with negligible electronic contribution. The ionic conductivities σ_i and activation enthalpies E_A are given in the following table.

	$\sigma_i\,[\Omega^{-1}\mathrm{cm}^{-1}]$						E_A [eV]
	25°C	50°C	100°C	200°C	300°C	400°C	
$Li_{1.8}N_{0.4}Cl_{0.6}$	$2.5x10^{-6}$	$9.5x10^{-6}$	$8.0x10^{-5}$	$8.4x10^{-4}$	$5.8x10^{-3}$	$2.2x10^{-2}$	0.49
$Li_{11}N_3Cl_2$	--	--	--	$2.8x10^{-6}$	$1.0x10^{-4}$	$2.4x10^{-3}$	0.83
$Li_{13}N_4Br$ (LT)	--	--	$2.0x10^{-7}$	$2.4x10^{-5}$			0.73
$Li_{13}N_4Br$ (HT)					$1.4x10^{-3}$	$4.5x10^{-3}$	0.47
Li_6NBr_3	--	$3.1x10^{-7}$	$2.0x10^{-6}$	$4.6x10^{-5}$			0.46

Recent measurements also indicate high ionic conduction in the lithium nitride iodides. Transference experiments have confirmed the motion of lithium ions.

All ternary compounds are stable against lithium. The thermodynamic decomposition voltage is always considerably larger than for Li_3N, e.g.,> 2.5 V for lithium nitride chloride, $Li_{1.8}N_{0.4}Cl_{0.6}$, which has an anti-fluorite structure with 10 % lithium vacancies.

The investigated materials are considered to be of potential interest in practical applications.

DEFECT PROPERTIES AND IONIC TRANSPORT IN LITHIUM NITRIDE*

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We present the results of a computationally based investigation of the mechanism of ion motion in the layer structured superionic Li_3N. The calculations employ ionic model potentials with short-range interactions represented by simple analytical potentials of the Born-Mayer forms; a shell model treatment of ionic polarisation is included. The variable parameters of this model are adjusted so as to reproduce the measured elastic and dielectric properties of the crystal.

Our calculations, which use the HADES[1] defect simulation program, show that the superionic properties of this material are a consequence of very high lithium vacancy mobilities: a value of 0.5 eV is calculated for vacancy jumps between layers, and an even lower value of 0.1 eV is obtained for in-plane vacancy migration. Moreover our results find very low values for the Li^+ Frenkel energy for this crystal, suggesting that thermally generated defects could play a significant role in the conduction mechanism in Li_3N.

Our results are compatible with the available experimental data. They suggest that the superionic properties of this material are a consequence of the unique type of layer structure adopted by Li_3N.

* Supported by UKAEA and Commission of the European Communities.

[1] UKAEA report AERE-R7650

PC-24

INTERSTITIAL SITES AND ANHARMONIC THERMAL VIBRATIONS IN THE CRYSTAL STRUCTURE OF LITHIUM NITRIDE (Li_3N)

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The crystal structure of Li_3N may be described as a sequence of Li- and Li_2N-layers perpendicular to the hexagonal c axis. Crystallographic nonequivalent Li(1) and Li(2) ions form the pure Li- and the Li_2N-layers.

Diffraction studies up to 620°C revealed, that the Li(2) ions play a peculiar role in this structure: They show a vacancy concentration of 1-2% already at room temperature. The high lithium conduction is evidently caused by jumps of Li(2) ions from an occupied site to an unoccupied site. The precursors of these jumps are strong anharmonic thermal vibrations of the Li(2) ions within and perpendicular to the Li_2N layers. These vibrations mark the directions of flat potentials and thereby the diffusion paths of the Li(2) ions.

Above 400°C the Li(2) ions start to form dynamical microdomains with a new lithium arrangement. At 600°C 15% of the Li(2) ions occupy the corresponding interstitial sites, which lie on the lithium conduction paths within the Li_2N layers.

Our investigation demonstrate, that the analysis of thermal vibrations yields valuable information on the probability of ionic conduction in a crystal. These vibrations mark the nets of flat potentials necessary for fast movements of ions through the lattice.

TEMPERATURE DEPENDENCE OF THE CRYSTAL STRUCTURE OF THE ONE-DIMENSIONAL Li^+-CONDUCTOR β-EUCRYPTITE ($LiAlSiO_4$)

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β-Eucyptite shows a very high Li^+ conductivity of one-dimensional character especially at high temperatures. At 600°C parallel to the hexagonal c-axis a conductivity of about 10^{-1} $[\Omega\ cm]^{-1}$ has been measured /1/.

At temperatures above 482°C $LiAlSiO_4$ crystallizes in a high-quartz structure (space group $P6_222$ or $P6_422$) with a doubled c lattice constant due to the ordered distribution of Al and Si. The charge compensating Li^+-ions are situated in structural channels parallel to c. By means of neutron diffraction the Li^+ distribution within these channels has been investigated. In the disordered high temperature phase Li^+ ions occupy only the two symmetrically independent sites of tetrahedral oxygen coordination with a probability ratio of three to one.

Below 482°C an ordering of the Li^+ in neighbouring channels leads via a modulated type of structure to the room temperature modification of β-Eucryptite, which is characterized by doubled a and b lattice constants. The phase transition does not affect the Li^+ conductivity. With decreasing temperature a distortion of the Li^+ distribution along the channels reduces their mobility.

/1/ U. v. Alpen, E. Schönherr, H. Schulz and G. H. Talat,
Electrochimica Acta 22, 805 (1977).

PC-26

DYNAMIC CAGE EFFECT: COMPARISON BETWEEN α-$RbAg_4I_5$ AND α-AgI

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In fast ion conductors, diffusion is a highly correlated process. In particular, the repulsive Coulomb interaction between the mobile ions generates a dynamic cage around each of them. The motion within the cage causes the characteristic very-far-infrared absorption and the broad component of quasielastic neutron-scattering spectra. Translational diffusion occurs since shape and position of the cage itself vary in time. The effective potential experienced by a mobile ion is essentially the sum of the dynamic cage-effect potential and a periodic one caused by the immobile ions. The examples of α-$RbAg_4I_5$ and α-AgI are chosen to demonstrate the influence of different barrier heights between neighboring tetrahedral sites on the motion of the silver ions in and with their cages.

In the case of α-$RbAg_4I_5$, at 295 K, we present the entire complex-conductivity spectrum along with the current-current correlation function. The data are consistent with the neutron-scattering results of Shapiro et al.. Within its cage a silver ion not only oscillates about its tetrahedral site, but also performs "trial-and-error" hops to neighboring sites. After an initial hop the back-hop probability is roughly 2/3. In 1/3 of all cases a new cage-potential minimum is dug at the new tetrahedral site.

In α-AgI, the situation is more liquid-like. Here, a silver ion moves relatively irregularly within its cage, which typically has a diameter of $\gtrsim 2$ Å and hence comprises more than one tetrahedral site. New single-crystal quasielastic neutron-scattering spectra do not indicate a pronounced anisotropy of this motion. The forward correlation of the translational motion of different silver ions as known from the Haven ratio and the microwave spectrum, is discussed in terms of the cage effect.

IONIC CONDUCTIVITY OF HOLLANDITE: A MODEL SYSTEM FOR THE TRANSPORT IN A ONE-DIMENSIONAL SYSTEM

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Various authors have presented evidence for ionic motion in the one-dimensional hollandite structure. Yet the published dc and ac conductivities obtained from polycrystalline samples differ by orders of magnitudes.

We have investigated the frequency dependent conductivity of single crystal hollandites of various compositions in the range from 5 Hz to 10 MHz and for temperatures between 77 K and 310 K. Our results lead to a comprehensive understanding of the transport processes in this one-dimensional ionic conductor. Our principal conclusions are:

a) the conductivity exhibits an anomalous dispersion of the type $\sigma \sim (i\omega)^{\alpha}$, $0 \leqslant \alpha \leqslant 1$; it is completely dominated by the existence of crystal defects imposing a wide spectrum of barriers on the ions moving within the channels. This is a true dimensionality effect.

b) The anisotropy of the intrinsic dc conductivity is in excess of 10^6, in any real sample the dc conductivity is thus completely suppressed.

c) The intrinsic conductivity within an unperturbed channel segment is $\sim .1$ $(\Omega\text{cm})^{-1}$ in agreement with a microscopic model based on structural data.

d) The ionic motion within a channel is a cooperative phenomenon, a single jump involves the coordinates of several ions; the intrinsic damping of the system, however, precludes any soliton-like free propagation.

PC-28

A ONE DIMENSIONAL SODIUM ION CONDUCTOR

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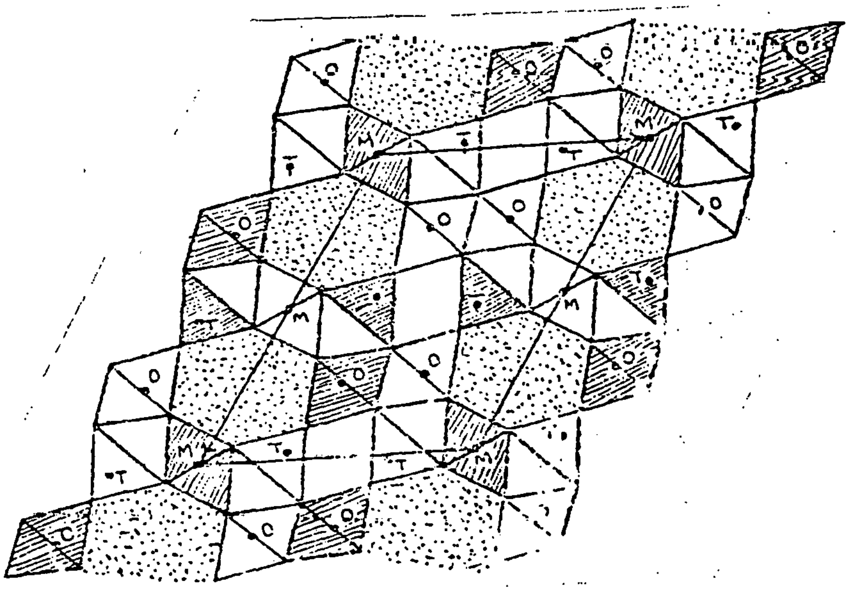
High one dimensional Na^+ ion conductivity has been observed in Ti substituted sodium gallate. This phase, a new structure type, is monoclinic (C_{2h}^3–C2/m) with unit cell dimensions of a=12.363, b=3.002, c=9.362A, β=122.09° and contains one dimensional channels parallel to b. In the b-axis projection oxygen polyhedra having their central metal atom at y=1/2 are cross-hatched while those at y=0 are unhatched. The cross section of the conducting channels are the dotted areas. The Na^+ ion electron density in the 1-D channels is continuous but not uniform. Single crystal a.c. and d.c. measurements indicate substantial ionic conductivity - parallel to the channel direction - of $\sigma>10^{-3}\Omega^{-1}cm^{-1}$ at 300°C with low activation energy and negligible electronic conductivity. Thermal analysis from room temperature to 1300°C reveals no phase transitions. Crystallographic, electrical and ion exchange characteristics and composition ranges will be detailed.



ATOM	No. SITES	SITE SYM.	OXYG. COORD. POLYHEDRA	<Metal-oxygen> distanceÅ
Ga 1	4	m	(T)etrehedral	1.841
Ga 2	4	m	(O)ctahedral (distorted)	1.997
Ga 3	2	2/m	(M)ixed octahedral	1.995

IONIC CONDUCTIVITY IN SHEET OXIDES

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A new class of alkali ionic conductors with sheet structures has been found. In particular, the two families $A_x(L_xM_{1-x})O_2$ (L = In, Sc ; M = Zr, Hf, Sn, Pb) and $A_x(L_{x/2}Sn_{1-x/2})O_2$ (L = Mg, Ca, Zn) (A = Na, K) ($x \leq 1$) have been studied.

In all these new layered materials the lattice is built up by sheets of edge-sharing $(L, M)O_6$ octahedra between which the alkali ions are inserted, with trigonal prismatic environment for small values of x and octahedral environment for larger ones.

The conductivity has been derived from complex impedance measurements. The mobility of the alkali ions can be discussed on the basis of their environment, the vacancy content and the electronegativity of the L and M elements.

The results show that the mobility is strongly correlated to the environment of the alkali ions : when the mobile ion is in a trigonal prismatic site the conductivity is 10^3 or 10^4 higher than when it is in an octahedron. The variation of the ratio of the A-O distance during the diffusion mechanism to the A-O distance when the alkali ion is in its normal site can explain this difference in behavior.

PC-30

EVIDENCE FOR PROTON CONDUCTIVITY IN COMPOUNDS IN THE HYDROGEN - URANYL - PERIODATE - WATER SYSTEM

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We have carried out studies on some phases in the hydrogen - uranyl - periodate - water system and have shown some of them to have comparable conductivities to the proton conductors hydrogen uranyl phosphate and arsenate tetrahydrates (1,2) (HUP and HUAs respectively). We have prepared phases of general formula $H_{5n-2}UO_2(IO_6)_nYH_2O$ in the composition range n = 0.5 - 2.0 in an attempt to produce structures which may be similar to HUP and HJAs. At least two crystalline phases have been found which have the approximate compositions $H(UO_2)_2IO_68H_2O$ and $H_8UO_2(IO_6)_24H_2O$ these have the conductivities 3×10^{-6} ohm^{-1} cm^{-1} and 7×10^{-3} ohm^{-1} cm^{-1} respectively at 293°K. The high conductivity of $H_8UO_2(IO_6)_24H_2O$ is thought to be associated with the large number of protons, of which there are too many to protonate the $(IO_6)^{5-}$ groups. This allows for the possibility of a residual high H^+ or H_3O^+ concentration which is known to occur also in HUP and HUAs. The low conductivity of $H(UO_2)_2IO_68H_2O$ may be explained by attachment of the single proton to the $(IO_6)^{5-}$ group to form $(IO_5OH)^{4-}$. At intermediate compositions in the approximate range n = 1-2, nonstoichiometric transparent glassy phases are formed which are X ray amorphous, some of these have conductivities above 10^{-3} ohm^{-1} cm^{-1} at 293°K and can easily be fabricated into thin flexible adherent films suitable for solid electrolyte applications. A comparison has been made between the potential uses of these materials and those of HUP and HUAs which have been used in devices such as electrochromic cells and batteries (3).

(1) M.G. SHILTON AND A.T. HOWE, Mat. Res. Bull. 12, 701, (1977).
(2) A.T. HOWE AND M.G. SHILTON, J. Solid St. Chem. 28, in press (1979)
(3) P.E. CHILDS, A.T. HOWE AND M.G. SHILTON, J. Power Sources, 3, 105 (1978).

PC-31

Sup

PROTONIC CONDUCTION OF HYDROGEN IMPURITIES IN $K_2O_sCl_6$*

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We report dielectric measurements as a function of temperature and frequency in single crystal $K_2O_sCl_6$ with defects containing protons. The results are consistent with a model which assumes the defect state to be a simple interstitial proton which is hydrogen bonded to the nearest neighbor chlorine ions. We find for temperatures greater than 180 K, that proton diffusion is thermally activated with a mobility of $10^{-2}cm^2/V$-sec whereas below this temperature it is determined by quantum tunneling between localized states.

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PC-32

ANHYDROUS DEUTERIUM BETA ALUMINAS

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Anhydrous polycrystalline hydrogen beta aluminas may be prepared by direct hydrogenation of silver beta aluminas. Preparations using single crystals are difficult and, if exchange is continued to near completion, there is extensive degradation of the crystals. Neutron diffraction of polycrystalline deuterium beta alumina is, therefore, the only practical method for structural study of the anhydrous hydrogenated material.

Apparently stoichiometric $DAl_{11}O_{17}$ is formed from non-stoichiometric sodium and silver precursors. In a first sample at low temperature, the deuterium was found to lie in the mirror plane, about 1Å from O(5), with approximately three-fold disorder around O(5). The Beevers-Ross, and other sites normally occupied by metal ions are empty. A second sample had, again, D-O(5) bonding but D is displaced off the mirror plane and there is a rotation of the (x,y) positions. The structure is dependent on the thermal history and a disordered arrangement with a c-axis shortening, observed on heating the first sample to 550°C, is preserved on cooling. The evolution of the deuterium arrangement with temperature from 4.2K to 450°C for the second sample is described.

Deuterium beta alumina samples have been prepared between 300°C and 450°C. Surprisingly, beta double prime alumina partially decomposes under these conditions, but deuteration of silver beta double prime alumina powder may be accomplished at 200°C without decomposition.

PC-33

TEMPERATURE DEPENDENCE OF HAVEN RATIO IN SILVER BETA-ALUMINA*

Dup

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Measurements of Ag diffusivity (D) and ionic conductivity (σ) have been made on the same single crystals of silver beta-alumina with composition $1.23Ag_2O$-$11Na_2O_3$. The D values were obtained from the cation exchange rate of radiotracer Ag^{110} in molten $AgNO_3$ over $210^oC \sim 400^oC$. The σ measurements were made at an impedance bridge frequency of $3x10^5$ HZ over R.T. ~ 450^oC using sputtered silver electrodes. Both D and σ can be expressed as simple Arrhenius relations: $D=1.47 \times 10^{-4}(cm^2/sec) \exp [\frac{-4.05 \text{ (kcal/mol)}}{RT}]$; $\sigma T=1.58 \times 10^3 (ohm^{-1}cm^{-1}\ {}^oK) \exp [\frac{-3.77 \text{ (kcal/mol)}}{RT}]$. The Haven ratio ranges from 0.51 at 200^oC to 0.57 at 400^oC. The magnitude of these values is very close to the theoretical value of 0.6 for interstitialcy mechanism in two-dimensional honeycomb structure. However, the most interesting feature of our results is the temperature dependence of the Haven ratio, which is strikingly similar to the case of sodium beta-alumina.[1] This feature is ascribed to interaction among defects which can come about in the form of ion blocking and binding among mobile ions and/or charge compensating defects.[2]

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*Supported in part by the U.S. Department of Energy.

[1] K. K. Kim, J. N. Mundy, and W. K. Chen, J. Phys. Chem. Solids, to be published.

[2] D. Wolf, J. Phys. Chem. Solids, to be published.

PC-34

MODELS FOR ION-ION CORRELATION IN β ALUMINA COMPOUNDS

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We study, by X ray diffraction (Bragg) and X ray diffuse scattering, the relation between local order and ionic conductivity in alumina type compounds : β_{Na}, β_{K}, β_{Tl} alumina (11 Al_2O_3, x B_2O, $x \simeq 1.25$) with charge compensation by interstitial oxygen. These compounds show two kinds of local behaviour :

1/ Na β alumina with very high Debye-Waller coefficients (∿ 1 Å) especially between mO and aBR sites. Short range order calculations indicate, in this case, a mixture of substitution disorder and of displacive disorder (probably dynamic). These local parameters are characterised (in static description) by the occurence of two types of ion-ion correlations.

Type I with a cluster of six Na ions on mO sites around a vacant aBr site and a very short correlation length (10 - 20 Å).

Type II with an order of both BR and mO ions

Our calculations introduce a correlated displacive parameter between ions of the same kind. This type of behaviour, highly disordered, accounts for the high ionic conductivity of Na β alumina.

2/ K and Tl β alumina with a local order in microdomains. In each domain, we observe the simultaneous occurence of different kinds of cells but all with Na type II order.

Owing to the higher ion-ion correlation lengths (40 - 50 Å) the ionic conductivity is considerably weaker. At a given temperature, a relation is observed between the size of the ordered regions, the ionic radius of the conduction ion and the activation energy.

X RAY STUDIES OF β AND β" ALUMINA WITH HIGH CONDUCTION ION CONCENTRATION

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In the system Al_2O_3-MgO-M_2O (M = Na, K, Ag), β" and β alumina single crystals can be obtained with a M^+ ions concentration of about 1.6 per unit cell within the conduction plane (instead of 1.25 for β alumina in the Al_2O_3-M_2O system).

- In β''_{Ag}, the silver ions are very weakly correlated in the conduction plane ($\xi < 10$ Å at 300 K) leading to a quasi liquid state between 20 and 300 K. A strong interplanar correlation is further observed.
- On the contrary for β''_{Na} and β''_{K} a two-dimensional local superstructure $a\sqrt{3} \times a\sqrt{3}$ is observed in the conduction plane (Na β" correlation length 70 Å at 300 K). No correlation is found between the planes.
- Moreover in β''_{Na} the fast variation of correlation length versus temperature at T > 300 K provides an explanation for the special behavior of this compound (non linear variation of Log σT versus T^{-1}).

These β" crystals are compared to recently prepared ion-rich β alumina with the same composition.

Except for Ag^+, the sizes of the ordered regions in these compounds are greater than in the normal β alumina ones, although their conductivities are similar ; implying another conduction mechanism with strong correlation (caterpillar mechanism).

PC-36

IONIC CONDUCTIVITY IN Na^+, K^+, AND Ag^+ BETA" ALUMINA

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This paper presents measurements of ionic conductivity in single crystals of Na^+, K^+, and Ag^+ beta" alumina ($0.83M_2O \cdot 0.33MgO \cdot 5Al_2O_3$, M = Na, K, Ag). Na^+ and K^+ beta" alumina have extremely high conductivities at 25°C, 0.16 $(ohm\ cm)^{-1}$ and 0.13 $(ohm\ cm)^{-1}$, respectively. The activation energies of all three materials were observed to decrease with increasing temperature, from 0.2 eV at 25°C to 0.1 eV at 400°C for Na^+ and K^+ beta" alumina, and from 0.22 eV at 25°C to 0.18 eV at 400°C for Ag^+ beta" alumina. The conductivity of Ag^+ beta" alumina at 25°C is $1.7 \cdot 10^{-3}$ $(ohm\ cm)^{-1}$.

Na^+ beta" alumina crystals were grown at 1660-1710°C from a melt containing Na_2O, Al_2O_3, and MgO. Selected crystals were converted to the potassium and silver isomorphs by ion exchange. Conductivity was measured as complex impedance with Au electrodes from -80°C to 500°C. Conductivity was observed to vary with conditions of crystal growth.

Few conductivity measurements on single crystals of beta" alumina have been reported. Our data are consistent with earlier work on Na^+ beta" alumina in which a conductivity of 0.06 $(ohm\ cm)^{-1}$ at 25°C and a decreasing activation energy were measured.[1]

These measurements have uncovered several intriguing phenomena such as the non-constant activation energy, the unusually high conductivity of K^+ beta" alumina and low conductivity of Ag^+ beta alumina, and the variations of conductivity with crystal growth conditions. A structural comparison of beta and beta" alumina begins to explain some of these effects.

[1] J.T. Kummer, Progress in Solid State Chemistry, Vol. 1, H. Reiss and J.O. McCaldin, ed., Pergamon Press, New York, 1972, p. 150.

CHARACTERIZATION OF NH_4^+ EXCHANGED SINGLE CRYSTAL β-ALUMINA

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A thorough characterization study is described of a large (∿ 3 cm diameter x 0.3 cm thickness) single crystal slice of NH_4^+ β-alumina prepared by ion exchange from the Na^+ analogue in molten ammonium nitrate.

Measurements of ionic conductivity (parallel to the mirror planes) using a.c. techniques and complex plane analysis lead to a good straight line plot of σT versus T^{-1} in the temperature range 300K-500K. Conductivities at 300K and 500K are $1.8.\ 10^{-6}\ \Omega^{-1}cm^{-1}$ and $1.4.\ 10^{-3}\ \Omega^{-1}cm^{-1}$ respectively with a corresponding activation energy of 0.47 eV. Similar measurements on a slice section (parallel to the c-axis) indicate a much lower conductivity in this direction. Above 500K, deviations from Arrhenius behaviour occur and the conductivity becomes time dependent until eventually steady but low values are recorded above about 800K. Preliminary measurements of conductivity from 800K to 1000K are also presented.

An unsupported sample undergoes severe delamination parallel to the mirror planes below 600K. D.T.A. experiments on similar material from 300K to 1500K indicate three major exothermic events at 800K, 1050K and 1300K and material annealed at various temperatures up to and between these points has been characterized by lattice parameter measurements using X-ray diffraction.

PC-38

HIGH RESOLUTION ELECTRON MICROSCOPY
STUDIES OF β- AND β"-ALUMINAS*

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Crystals of β- and β"-alumina have been investigated by means of high-resolution transmission electron microscope with a maximum resolution at 2.7 Å. Experimentally-obtained crystal structure images are compared with computer simulated images in order to arrive at a correct interpretation.

The crystals here studied are both long-cycled battery ones as well as newly prepared. All crystals of β"-aluminas investigated so far revealed two types of defects. Two broad close-packed Al-O-slabs can cause a blockage of the ion-conducting layers in the solid electrolyte. It is shown how two slabs of different width always have the same type of blocking junction. Growth of broad Al-O-slabs under the influence of the electron beam was recorded in β"-aluminas but not in β-aluminas. The growth always starts in the crystals and travels out to the edge. The broad Al-O-slabs grow only of the thickness (4N + 1) × 2.2 Å. Possible mechanisms for the growth of broad Al-O-slabs are suggested. The importance of the defects for understanding of material problems of conducting Na-S-batteries with β- and β"-alumina is discussed.

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ELECTRON SPIN RELAXATION BY TUNNELING STATES IN Na-β-Al_2O_3*

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We have measured the spin relaxation rate of an F^+ color center in the conduction plane of Na-β-Al_2O_3 and found an anomalous temperature and microwave frequency dependence. In addition the rate was two to three orders of magnitude faster than that usually observed for color centers in ordered ionic materials. The observed behavior is quantitatively described by a relaxation mechanism involving the coupling of a color center to the phonon induced relaxation of a nearby localized two level tunneling state. These states are associated with disorder in the conduction plane of Na-β-Al_2O_3 and have been used to explain the low temperature properties of beta aluminas and other amorphous materials.1/ The F^+ relaxation mechanism is analogous to the enhancement of nuclear relaxation rates in the presence of paramagnetic impurities. Using tunneling state parameters determined by thermal and dielectric measurements on Na-β-Al_2O_3, this mechanism predicts relaxation rates for the F^+ centers consistent with the experimental data. Assuming a density of localized tunneling states similar to that used to interpret the low temperature properties of Na-β-Al_2O_3, this theory yields the temperature dependence observed in our data.

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1/ P. J. Anthony and A. C. Anderson, Phys. Rev. (to be published)

AUTHOR INDEX

Author Index

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