

AD-A125 066

ELECTRICAL RELAXATION IN RARE EARTH DOPED CUBIC LEAD
FLUORIDE(U) CASE WESTERN RESERVE UNIV CLEVELAND OHIO
DEPT OF PHYSICS J J FONTANELLA ET AL. NOV 82 TR-5
N00014-83-AF-00001 F/G 20/3

1/1

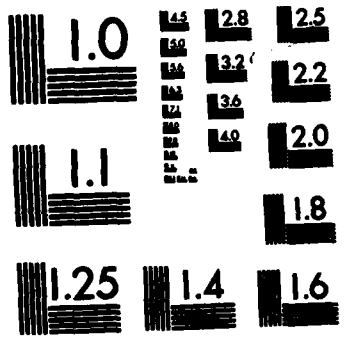
UNCLASSIFIED

NL

END

FORM

DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD A1 25006

OFFICE OF NAVAL RESEARCH

Contract N00014-83-AF-00001

Task No. NR 627-793

TECHNICAL REPORT NO. 5

Electrical Relaxation in Rare Earth

Doped Cubic Lead Fluoride

by

John J. Fontanella and Mary C. Wintersgill

Prepared for Publication

in

Radiation Effects

U. S. Naval Academy
Department of Physics
Annapolis, MD 21402

November 1982

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited

DTIC
ELECTE
S **D**
FEB 28 1983
E

DTIC FILE COPY

88 02 028 011

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 5	2. GOVT ACCESSION NO. AD-A125066	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) ELECTRICAL RELAXATION IN RARE EARTH DOPED CUBIC LEAD FLUORIDE		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) John J. Fontanella and Mary C. Wintersgill		8. CONTRACT OR GRANT NUMBER(s) N0001483AF00001 ^ ^ ^
9. PERFORMING ORGANIZATION NAME AND ADDRESS Physics Department U. S. Naval Academy Annapolis, MD 21402		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR No. 627-793
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Attn: Code 413, 800 N. Quincy St. Arlington, VA 22217		12. REPORT DATE November, 1982
		13. NUMBER OF PAGES 8
14. MONITORING AGENCY NAME & ADDRESS (If different from Controlling Office)		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale. Its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES To be published in "Radiation Effects"		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Solid electrolytes, fluorine ion conductor, lead fluoride, electrical relaxation spectroscopy		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Audio frequency complex impedance measurements are performed over the temperature range 5.5-380K on lead fluoride doped with ten rare earths and lanthanum at various concentrations. It is found that the complexity of the relaxation spectrum increases as the size of the trivalent ion decreases. Specifically, for the largest rare earths, only one relaxation is found. That relaxation is different from the cases in the alkaline earth fluorides where only one relaxation is observed in that the		

Block 20 - Abstract continued
 reorientation enthalpy depends strongly upon ion size. Double-doped samples are studied to determine whether the relaxation is due to a simple site or a cluster. For the smallest rare earths, however, at least nine relaxations are found. The concentration studies indicate multiple relaxations for certain sites. Both simple sites and clusters are observed for small rare earths.

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	



Lattice Defects in Ionic Crystals, 30 August-5 September 1982,
Dublin, Ireland. The paper will appear in Radiation Effects.

ELECTRICAL RELAXATION IN RARE EARTH DOPED CUBIC LEAD FLUORIDE*

M.C. WINTERGILL, J.J. FONTANELLA, F.P. PURSEL
Physics Department, U.S. Naval Academy, Annapolis, MD 21402, USA

and

A.V. CHADWICK, A. AZIMI, V.M. CARR
University Chemical Laboratory, University of Kent at Canterbury, Canterbury,
Kent, UK

and

C.G. ANDEEN
Physics Department, Case Western Reserve University, Cleveland, OH 44106
USA

ABSTRACT

Audio frequency complex impedance measurements are performed over the temperature range 5.5-380K on lead fluoride doped with ten rare earths and lanthanum at various concentrations. It is found that the complexity of the relaxation spectrum increases as the size of the trivalent ion decreases. Specifically, for the largest rare earths, only one relaxation is found. That relaxation is different from the cases in the alkaline earth fluorides where only one relaxation is observed in that the reorientation enthalpy depends strongly upon ion size. Double-doped samples are studied to determine whether the relaxation is due to a simple site or a cluster. For the smallest rare earths, however, at least nine relaxations are found. The concentration studies indicate multiple relaxations for certain sites. Both simple sites and clusters are observed for small rare earths.

INTRODUCTION

Lead fluoride presents a number of interesting differences in its properties as compared with isostructural materials such as the alkaline earth fluorides. In addition to a surprisingly large low frequency dielectric constant which decreases with temperature,¹ it exists in two different structures at room temperature and pressure.^{2,3} Having a relatively low superionic transition temperature,⁴ it has been considered as a candidate for solid electrolyte applications, and therefore the electrical properties of both pure and doped lead fluoride are of considerable interest, and some significant results have been obtained.⁵⁻⁷ The present work is concerned with cubic lead fluoride doped with ten rare earths, lanthanum and the results are compared with similar studies of alkaline earth fluorides.

EXPERIMENTAL PROCEDURE

Single crystals of cubic lead fluoride doped with ten rare earths, lanthanum and yttrium, including six different concentrations of erbium were prepared by the Stockbarger technique⁸ and complex impedance measurements at temperatures between 5.5K and 380K were performed, as described previously.⁹ For each sample, the results were transformed to the complex dielectric constant $\epsilon^* = \epsilon' - \epsilon''$ using techniques described elsewhere¹⁰ and the values of the linear thermal expansion coefficient used were for pure PbF_2 ¹¹ due to a lack of values for rare earth doped lead fluoride.

RESULTS AND DISCUSSION

Rare Earths larger than Gd

There is a striking variation in the dielectric relaxation spectrum, as the dopant ion size changes, as shown in Fig. 1. For larger dopants than gadolinium, in samples with 0.1% dopant, the spectrum is dominated by a single relaxation peak which is considerably stronger than any of the relaxations seen in the AEF. The activation energy of this peak changes steadily by about .04 eV per rare earth from approximately 0.4 eV for La to about 0.1 eV for Gd. This type of behavior has been observed in studies of the alkaline earth fluorides (the R_{IV} relaxation observed in CaF_2 , SrF_2 but not in BaF_2), for a relaxation associated with two rare earths, specifically the "gettered 2:2:2" cluster.^{12,13} In lead fluoride, however, it is the only relaxation observed for large rare earths in contrast to the AEF where at least one other peak is always seen. Thus, it is considered unlikely that the only peak in lead fluoride at the 0.1% doping level should be associated with more than one rare earth. This is supported by the concentration studies which show that from 0.1 to 1.0 mol-% the 70K peak grows at the expense of the 50K peak.

In an effort to clarify this point, the dielectric spectrum of a sample doped with 0.05% each of La and Gd was taken, and is shown in Fig. 2 together with those of La- and Gd-doped samples. The spectrum for the double doped sample is dominated by the same two relaxations (180K, 55K) as are seen in the La- and Gd-doped samples. No corresponding "hybrid" relaxation peak involving both types of dopant ions is observed. Such a peak would be larger in magnitude than the single dopant peaks, and on the basis of earlier AEF studies, the position would be expected to

be close to the Gd peak.¹⁴ This confirms that the single dominant peak seen for large rare earths is due to a simple center. However, as can be seen in Figure 2, several hybrid peaks are observed in the double doped sample (30, 80, 135K). These correspond to the small relaxations observed in the Gd-doped material (20, 75, 100K). There is no evidence of such relaxations in the La-doped material.

Two of the three hybrid peaks (30, 135K) are indeed of larger size than the Gd peaks and are close to the positions of the smaller dopant relaxations. In addition, studies of a different dopant concentration indicate that those peaks increase in height with increased dopant concentration. Therefore, these peaks are associated with centers containing at least two rare earth ions.

For the remaining peak, that at 75K, the possible hybrid peak, that at 80K, is very weak. However, the concentration studies indicate that the 75K peak may be due to the same center as the 20K peak. Thus, since multiple relaxations per site have already been identified in this material and since no analogous relaxation is observed in the La-doped material, it is not surprising that a separate, strong, hybrid peak is not observed for the 75K peak.

Rare Earths Smaller than Gd

As the size of the dopant ion decreases, the complexity of the relaxation spectrum increases, as is the case in the alkaline earth fluorides. The relaxation spectra of five samples doped with small RE's are shown in Figure 1. As an example, nine different peaks can be identified in different concentrations of Er-doped PbF_2 as was shown in a previous paper.⁹ The assignments in that work of two peaks, α_1 ,

(10K and 15.6K) associated with a simple center and three peaks, β_1 , (30K, 70K and 160K) associated with a simple cluster, agree with the selective laser excitation work of Mho and Wright.¹⁵ Of the simple clusters, the peak labeled β_3 at 160K shows a clear dependence on ion size. Thus, it may be that the β relaxations are associated with the "gettered" 2:2:2. Another peak, δ (116K) was also identified as a cluster. The same laser work¹⁵ indicates that the peak labeled γ (50K) and designated as due to a simple cluster in the previous paper⁹ is in fact associated with a single dopant ion, although it does reach maximum peak height at a higher concentration than those labeled α . The concentration dependence must therefore be due to some other effect such as reduction of strain energy. Finally, further analysis of the results has yielded a new peak, η , on the high temperature side of the α_2 peak, (about 19K) which is most prominent at the higher concentrations, suggesting that it too is a cluster of some kind.

The positions of both the peaks due to simple centers and some of the cluster associated centers are unusually low in temperature when compared with the alkaline earth fluorides. This may be due partly to the high polarizability of the lead ion or may even indicate that some of these relaxations involve electronic motion. This latter possibility is supported by evidence from other experiments of the existence of electronic contributions to the conductivity of lead fluoride.⁵

REFERENCES

1. G. A. Samara, *Phys. Rev.* B13, 4529 (1976).
2. G. A. Samara, *J. Phys. Chem. Solids*, 40, 509 (1979).
3. J. Oberschmidt and D. Lazarus, *Phys. Rev.* B21 2952 (1980).
4. W. Schröter and J. Nölting, *J. de Phys.*, 41 C6-20 (1980).
5. R. W. Bonne and J. Schoonman, *J. Electrochem. Soc.* 124, 28 (1977).
6. V. M. Carr, A. V. Chadwick and R. Saghafian, *J. Phys. C.*, 11, L637 (1978).
7. R. E. Gordon and J. H. Strange, *J. Phys. C.*, 11, 3213 (1978).
8. D. R. Figueroa, A. V. Chadwick and J. H. Strange, *J. Phys. C.*, 11, 55 (1978).
9. J. J. Fontanella, M. C. Wintersgill, P. J. Welcher, A. V. Chadwick, A. Azimi, V. M. Carr, and C. G. Andeen, Proceedings of the Second European Conference on Solid State Chemistry, Veldhoven, The Netherlands, 7-9 June 1982, to be published.
10. C. Andeen, D. Link and J. Fontanella, *Phys. Rev.* B16 3762 (1977).
11. G. K. White, *J. Phys.*, C13, 4905 (1980).
12. C. G. Andeen, J. J. Fontanella, M. C. Wintersgill, P. J. Welcher, R. J. Kimble, Jr., and G. E. Matthews, Jr., *J. Phys.*, C14, 3557 (1981).
13. M. C. Wintersgill, J. J. Fontanella, P. Welcher, R. J. Kimble, Jr., and C. G. Andeen, *J. Phys.*, C13, L661 (1980).
14. C. G. Andeen, G. F. Matthews, Jr., M. K. Smith, and J. Fontanella, *Phys. Rev.*, B19, 5293 (1979).
15. S. I. Mho and J. C. Wright, private communication.

Figure 1. ϵ'' vs. $T(K)$ for various rare earths and lanthanum in lead fluoride at 10^4 Hz. The concentration is nominally 0.1 mol-%.

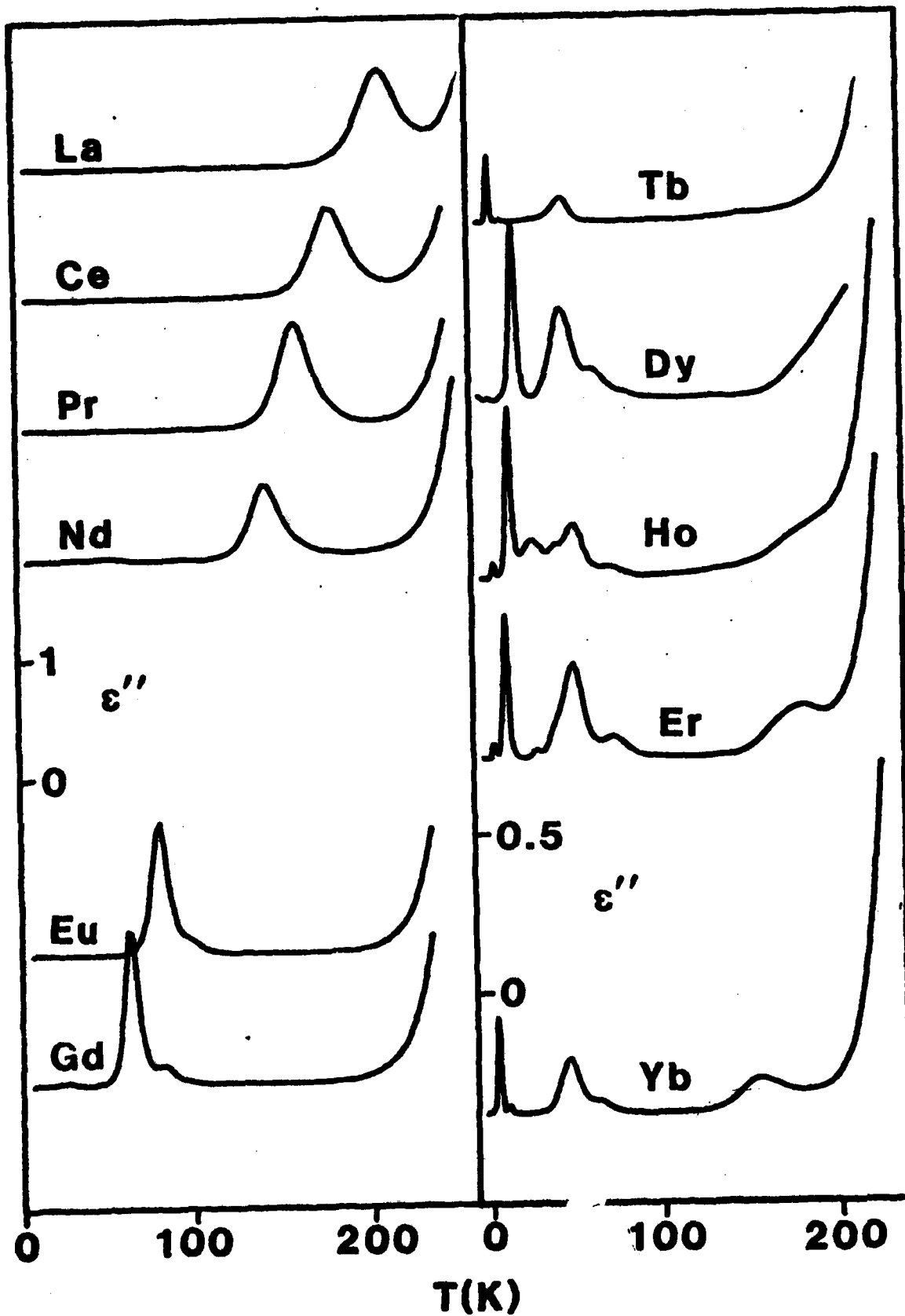
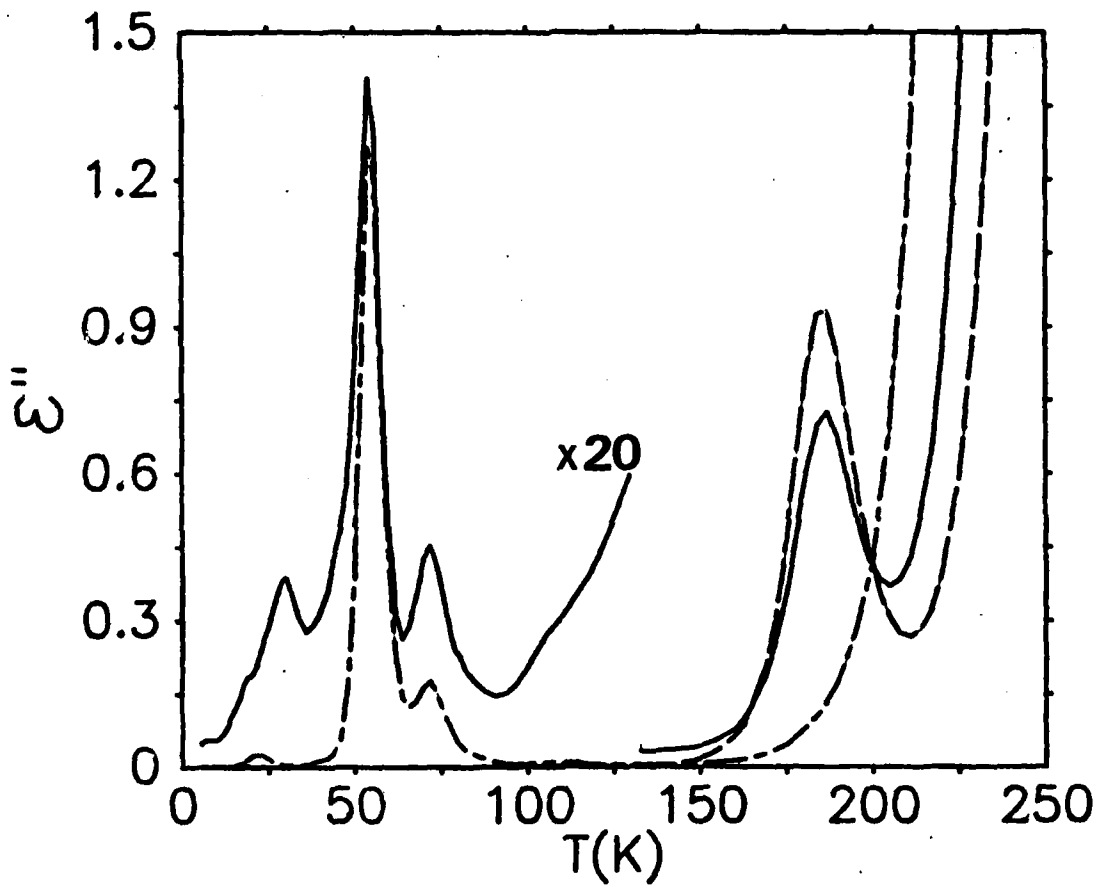


Figure 2. ϵ'' vs. $T(K)$ for 0.2 mol-% Gd (chain link), 0.1 mol-% La (dashed line), and 0.05 mol-% each of Gd and La (solid line) in lead fluoride at 10^3 Hz. (Data for double-doped material is multiplied by 20 for temperatures less than 130K.)



TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No Copies</u>
Office of Naval Research Attn: Code 413 800 North Quincy Street Arlington, Virginia 22217	2	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Pasadena Detachment Attn: Dr. R. J. Marcus 1030 East Green Street Pasadena, California 91106	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Dean William Tolles Naval Postgraduate School Monterey, California 93940	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
U.S. Army Research Office Attn: CRD-AA-IP P. O. Box 12211 Research Triangle Park, N.C. 27709	1	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Mr. Vincent Schaper DTNSRDC Code 2803 Annapolis, Maryland 21402	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1	Mr. A. M. Anzalone Administrative Librarian PLASTEC/ARRADCOM Bldg 3401 Dover, New Jersey 07801	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. Paul Delahay Department of Chemistry New York University New York, New York 10003	1	Dr. P. J. Hendra Department of Chemistry University of Southampton Southampton SO0 5NH United Kingdom	1
Dr. E. Yeager Department of Chemistry Case Western Reserve University Cleveland, Ohio 41106	1	Dr. Sam Perone Chemistry & Materials Science Department Laurence Livermore National Lab. Livermore, California 94550	1
Dr. D. N. Bennion Department of Chemical Engineering Brigham Young University Provo, Utah 84602	1	Dr. Royce W. Murray Department of Chemistry University of North Carolina Chapel Hill, North Carolina 27514	1
Dr. R. A. Marcus Department of Chemistry California Institute of Technology Pasadena, California 91125	1	Naval Ocean Systems Center Attn: Technical Library San Diego, California 92152	1
Dr. J. J. Auburn Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. C. E. Mueller The Electrochemistry Branch Materials Division, Research and Technology Department Naval Surface Weapons Center White Oak Laboratory Silver Spring, Maryland 20910	1
Dr. Adam Heller Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. G. Goodman Johnson Controls 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Dr. T. Katan Lockheed Missiles and Space Co., Inc. P. O. Box 504 Sunnyvale, California 94088	1	Dr. J. Boechler Electrochimica Corporation Attn: Technical Library 2485 Charleston Road Mountain View, California 94040	1
Dr. Joseph Singer, Code 302-1 NASA-Lewis 21000 Brookpark Road Cleveland, Ohio 44135	1	Dr. P. P. Schmidt Department of Chemistry Oakland University Rochester, Michigan 48063	1
Dr. B. Brummer EIC Incorporated 55 Chapel Street Newton, Massachusetts 02158	1		
Library P. R. Mallory and Company, Inc. Northwest Industrial Park Burlington, Massachusetts 01803	1		

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. H. Richtol Chemistry Department Rensselaer Polytechnic Institute Troy, New York 12181	1	Dr. R. P. Van Duyne Department of Chemistry Northwestern University Evanston, Illinois 60201	1
Dr. A. B. Ellis Chemistry Department University of Wisconsin Madison, Wisconsin 53706	1	Dr. B. Stanley Pons Department of Chemistry University of Alberta Edmonton, Alberta CANADA T6G 2G2	1
Dr. M. Wrighton Chemistry Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139		Dr. Michael J. Weaver Department of Chemistry Michigan State University East Lansing, Michigan 48824	1
Larry E. Plew Naval Weapons Support Center Code 30736, Building 2906 Crane, Indiana 47522	1	Dr. R. David Rauh EIC Corporation 55 Chapel Street Newton, Massachusetts 02158	1
S. Ruby DOE (STOR) 600 E Street Providence, Rhode Island 02192	1	Dr. J. David Margerum Research Laboratories Division Hughes Aircraft Company 3011 Malibu Canyon Road Malibu, California 90265	1
Dr. Aaron Wold Brown University Department of Chemistry Providence, Rhode Island 02192	1	Dr. Martin Fleischmann Department of Chemistry University of Southampton Southampton 509 5NH England	1
Dr. R. C. Chudacek McGraw-Edison Company Edison Battery Division Post Office Box 28 Bloomfield, New Jersey 07003	1	Dr. Janet Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. A. J. Bard University of Texas Department of Chemistry Austin, Texas 78712	1	Dr. R. A. Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. M. M. Nicholson Electronics Research Center Rockwell International 3370 Miraloma Avenue Anaheim, California	1		

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. Donald W. Ernst Naval Surface Weapons Center Code R-33 White Oak Laboratory Silver Spring, Maryland 20910	1	Mr. James R. Moden Naval Underwater Systems Center Code 3632 Newport, Rhode Island 02840	1
Dr. R. Nowak Naval Research Laboratory Code 6130 Washington, D.C. 20375	1	Dr. Bernard Spielvogel U. S. Army Research Office P. O. Box 12211 Research Triangle Park, NC 27709	1
Dr. John F. Houlihan Shenango Valley Campus Pennsylvania State University Sharon, Pennsylvania 16146	1	Dr. Denton Elliott Air Force Office of Scientific Research Bolling AFB Washington, D.C. 20332	1
Dr. D. F. Shriver Department of Chemistry Northwestern University Evanston, Illinois 60201	1	Dr. David Aikens Chemistry Department Rensselaer Polytechnic Institute Troy, New York 12181	1
Dr. D. H. Whitmore Department of Materials Science Northwestern University Evanston, Illinois 60201	1	Dr. A. P. B. Lever Chemistry Department York University Downsview, Ontario M3J1P3 Canada	1
Dr. Alan Bewick Department of Chemistry The University Southampton, SO9 5NH England		Dr. Stanislaw Szpak Naval Ocean Systems Center Code 6343 San Diego, California 95152	1
Dr. A. Himy NAVSEA-5433 NC #4 2541 Jefferson Davis Highway Arlington, Virginia 20362		Dr. Gregory Farrington Department of Materials Science and Engineering University of Pennsylvania Philadelphia, Pennsylvania 19104	1
Dr. John Kincaid Department of the Navy Strategic Systems Project Office Room 901 Washington, D.C. 20376		Dr. Bruce Dunn Department of Engineering & Applied Science University of California Los Angeles, California 90024	

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
M. L. Robertson Manager, Electrochemical and Power Sonics Division Naval Weapons Support Center Crane, Indiana 47522	1	Dr. T. Marks Department of Chemistry Northwestern University Evanston, Illinois 60201	1
Dr. Elton Cairns Energy & Environment Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	1	Dr. D. Cipris Allied Corporation P. O. Box 3000R Morristown, New Jersey 07960	1
Dr. Micha Tomkiewicz Department of Physics Brooklyn College Brooklyn, New York 11210	1	Dr. M. Philpot IBM Corporation 5600 Cottle Road San Jose, California 95193	1
Dr. Lesser Blum Department of Physics University of Puerto Rico Rio Piedras, Puerto Rico 00931	1	Dr. Donald Sandstrom Washington State University Department of Physics Pullman, Washington 99164	1
Dr. Joseph Gordon, II IBM Corporation K33/281 5600 Cottle Road San Jose, California 95193	1	Dr. Carl Kannewurf Northwestern University Department of Electrical Engineering and Computer Science Evanston, Illinois 60201	1
Dr. Robert Somoano Jet Propulsion Laboratory California Institute of Technology Pasadena, California 91103	1	Dr. Edward Fletcher University of Minnesota Department of Mechanical Engineering Minneapolis, Minnesota 55455	1
Dr. Johann A. Joebstl USA Mobility Equipment R&D Command DRDME-EC Fort Belvoir, Virginia 22060	1	Dr. John Fontanella U.S. Naval Academy Department of Physics Annapolis, Maryland 21402	1
Dr. Judith H. Ambrus NASA Headquarters M.S. RTS-6 Washington, D.C. 20546	1	Dr. Martha Greenblatt Rutgers University Department of Chemistry New Brunswick, New Jersey 08903	1
Dr. Albert R. Landgrebe U.S. Department of Energy M.S. 6B025 Forrestal Building Washington, D.C. 20595	1	Dr. John Wassib Kings Mountain Specialties P. O. Box 1173 Kings Mountain, North Carolina 28086	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No.</u> <u>Copies</u>	<u>No.</u> <u>Copies</u>
J. J. Brophy University of Utah Department of Physics Lake City, Utah 84112	1	
Walter Roth Department of Physics The University of New York New York, New York 12222	1	
Thomas Davis National Bureau of Standards Physical Science and Standards Division Gaithersburg, D.C. 20234	1	
Charles Martin Department of Chemistry Texas A&M University	1	
Anthony Samuels Institute of Gas Technology 3301 South State Street Chicago, Illinois 60616	1	
H. Tachikawa Department of Chemistry Mississippi State University Mississippi State, Mississippi 39217	1	
W. M. Risen Department of Chemistry Brown University Providence, Rhode Island	1	