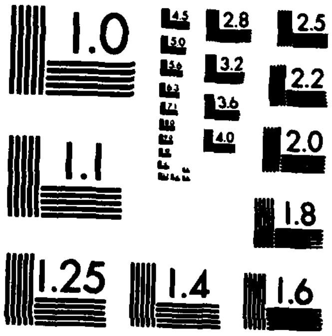
AD-A143 201 ANOMALOUS PRESSURE DEPENDENCE OF DIPOLAR RELAXATION 1/1
TIMES IN RARE EARTH DOPED LEAD FLUORIDE(U) NAVAL
ACADEMY ANNAPOLIS MD DEPT OF PHYSICS
UNCLASSIFIED J J FONTANELLA ET AL. MAY 84 TR-13 F/G 7/4 NL



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

①

OFFICE OF NAVAL RESEARCH

~~Contract N00014-84-AF-00001~~

Task No. NR 627-793

TECHNICAL REPORT NO. 13

ANOMALOUS PRESSURE DEPENDENCE OF DIPOLAR RELAXATION TIMES IN RARE EARTH DOPED LEAD FLUORIDE

by

John J. Fontanella & Mary C. Wintersgill

Prepared for Publication

in

Physical Review Letters

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

May 1984

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

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER
13

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
ANOMALOUS PRESSURE DEPENDENCE OF DIPOLAR RELAXATION TIMES IN RARE EARTH DOPED LEAD FLUORIDE

5. TYPE OF REPORT & PERIOD COVERED
Interim technical report

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
JOHN J. FONTANELLA & MARY C. WINTERSGILL

8. CONTRACT OR GRANT NUMBER(s)
[redacted]

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
May 1984

13. NUMBER OF PAGES
15

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)
Approved for public release and sale.
Distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
Solid electrolytes, fluorine ion conductors, lead fluoride, rare earths, high pressures, electrical relaxation.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Electrical relaxation measurements at high pressures have been carried out on lead fluoride doped with lanthanum and cerium. A single, strong relaxation peak is observed and the relaxation time decreases with pressure. This is contrary to the behavior exhibited by all known relaxations and can be explained by attributing the relaxation to a substitutional trivalent rare earth compensated either by an interstitial fluorine ion with a soft attempt mode or by an electron.

Anomalous Pressure Dependence of Dipolar Relaxation Times in Rare Earth Doped Lead Fluoride

J. J. Fontanella* M. C. Wintersgill* D. R. Figueroa+
A. V. Chadwick@ and C. G. Andeen#

* Physics Department, U. S. Naval Academy, Annapolis, Md 21402
\+ Universidad Simon Bolivar, Apartado 80659, Caracas, Venezuela.
@ University of Kent, Canterbury, Kent, England.
\# Case Western Reserve University, Cleveland, Ohio, 44106

ABSTRACT

Electrical relaxation measurements at high pressures have been carried out on lead fluoride doped with lanthanum and cerium. A single, strong relaxation peak is observed and the relaxation time decreases with increasing pressure. This is contrary to the behavior exhibited by all known relaxations and can be explained by attributing the relaxation to a substitutional trivalent rare earth compensated either by an interstitial fluorine ion with a soft attempt mode or by an electron.

will be discussed in detail elsewhere. For PbF_2:Ce, no conductivity correction was made and the results are quite similar to figure 2. The Cole-Cole expression was fitted to the data in order to determine the relaxation times at various pressures. The resultant relaxation times vs. pressure are shown in figure 3 for PbF_2:La and the slopes of the best fit straight lines for all samples are listed in Table 1. The decrease of relaxation time as pressure increases is opposite from that observed for any dipolar relaxation time studied to date including work on ionic crystals[17-20] or polymers.[21]

It may be that the anomalous pressure dependence of the relaxation time is another manifestation of the soft mode behavior which lead fluoride has been suggested to exhibit.[1,5] Specifically, it might be concluded that the usual reorientation of a charge compensating fluorine ion (IC) near a substitutional rare earth is taking place, and that the vibrational mode governing the reorientation is a soft mode. Possibly the best way to illustrate this is via the activation volume:

$$\Delta V^*_{exp} = kT \frac{\partial \mathrm{Ln}\, \tau}{\partial P}$$

which yields the negative values listed in Table 1. The dynamical diffusion theoretical expression[20]

$$\Delta V^*_{th} = 2\, \gamma_a \chi_T\, g$$

where χ_T is the compressibility and g is the Gibbs energy, then requires a negative attempt mode Gruneisen parameter, γ_a, indicating a soft mode, to explain the data.

However, these relaxations exhibit a very strong dependence of peak position or activation energy on dopant ion size as is evident from Table 1 for PbF_2:La and PbF_2:Ce and figure 1 of reference 9. It may be that the same spring constants which soften upon application of pressure also enhance the interaction between the RE and the reorienting fluorine interstitial. IC has the additional advantage of easily explaining the relatively high activation energies, 0.4 and 0.32 eV, observed for La and Ce. However, the activation energy for the analogous relaxation in PbF_2:Gd is very low, about 0.11 eV. This suggests an alternative interpretation of the data. The second model proposed is that the RE is charge compensated by an electron (EC) localized around one of the adjacent lattice fluorine ions. The decrease in the relaxation time with increased pressure would then be a result of increased electron wavefunction overlap between equivalent wells as pressure reduces the lattice parameter. Further, these same overlap effects will make the electronic relaxation time very sensitive to the extent of the RE's electron wavefunction and thus explain the variation of activation energy with ion size.

These models have the following implications concerning several other unusual features of the electrical response of RE doped PbF_2.

Firstly, the magnitude of the conductivity does not scale with the strength of the principal relaxation over the dopant range 0.1 to 1.0 mole% (nominal) in that the strength of the relaxation increases while the magnitude of the conductivity does not. This result favors the EC model since there should be no correlation of the strength of the relaxation and the magnitude of the conductivity which is primarily ionic.[22,23] (There have been reports of electronic contributions to the conductivity of lead fluoride[24,25] and this increases the plausibility of EC.) Of course, the IC model could explain the results if the association energy is so large that it is not the complex responsible for the extrinsic conductivity. In either case, another defect site must coexist with that responsible for the principal relaxation since the conductivity is well-behaved and can be fit via a classical association model.[22,23] In fact, a relatively weak relaxation is observed in both PbF_2:La and PbF_2:Ce at a slightly higher temperature than the principal relaxation. That is part of the reason for the poor fit of the data shown in figure 1. If that site has only a very small dipole moment the concentration could be sufficiently large to give rise to the extrinsic conductivity.

Secondly, the deviation of the relaxations from Curie-Weiss behavior can be understood either in terms of EC or IC. In the case of EC, it could easily be that the dipole moment increases as temperature increases. For either EC or IC a slight potential well inequivalency could also explain the trend.

Finally, there is the phenomenon of the existence of multiple low temperature relaxations per defect center observed for PbF_2 doped with RE's smaller than gadolinium.[8,9] This has not been observed in association with ionic relaxations in the AEF. Consequently, those results suggest the existence of at least some electronic compensation.

In summary, it has been shown that for the single, strong relaxation observed in PbF_2 doped with large RE's, the relaxation time decreases as pressure increases. By attributing the relaxation to an electronically compensated or soft mode related, fluorine interstitial compensated substitutional trivalent RE, this anomalous behavior, together with some previously unexplained phenomena, can be understood.

This work was supported in part by the Office of Naval Research.

REFERENCES

1. G. A. Samara, Phys. Rev. B13, 4529 (1976).
2. C. Andeen, D. Schuele, and J. Fontanella, Phys. Rev. B6, 591 (1972).
3. W. Schroter and J. Nolting, J. de Phys., 41, C6-41 (1980).
4. G. K. White, J. Phys. C13, 4905 (1980).
5. D. S. Rimai and R. J. Sladek, Phys. Rev. B21, 843 (1980).
6. J. Oberschmidt and D. Lazarus, Phys. Rev. B21, 2952 (1980).
7. G. A. Samara, J. Phys. Chem. Solids 40, 509 (1979).
8. J. J. Fontanella, M. C. Wintersgill, P. J. Welcher, A. V. Chadwick, A. Azimi, V. M. Carr, and C. G. Andeen, in Solid State Chemistry 1982, Studies in Inorganic Chemistry, Vol. 3, edited by R. Metselaar, H. J. M. Heijligers, and J. Schoonman (Elsevier Scientific, Amsterdam, 1983), p. 219.
9. M. C. Wintersgill, J. J. Fontanella, F. P. Pursel, A. V. Chadwick, A. Azimi, V. M. Carr, and C. G. Andeen, Radiation Effects, to be published.
10. N. Suarez, D. Figueroa, E. Laredo, and M. Puma, Crystal

Lattice Defects, 9, 207 (1982).

11. C. Andeen, D. Link, and J. Fontanella, Phys. Rev. B16, 3762 (1977).

12. C. G. Andeen, J. J. Fontanella, M. C. Wintersgill, P. J. Welcher, R. J. Kimble, Jr., and G. E. Matthews, Jr., J. Phys. C 14, 3557 (1981).

13. C. Andeen, G. E. Matthews, Jr., M. K. Smith, and J. Fontanella, Phys. Rev. B19, 5293 (1979).

14. D. R. Figueroa, A. V. Chadwick, and J. H. Strange, J. Phys. C 11, 55 (1978).

15. J. Fontanella, C. Andeen, and D. Schuele, Phys. Rev. B6, 582 (1972).

16. J. J. Fontanella, M. C. Wintersgill, P. J. Welcher, A. V. Chadwick, and C. G. Andeen, Solid St. Ionics 5, 585 (1981).

17. J. J. Fontanella, M. C. Wintersgill, and C. Andeen, Phys. Stat. Sol. (b) 97, 303 (1980).

18. C. G. Andeen, J. J. Fontanella, and M. C. Wintersgill, J. Phys. C 13, 3449 (1980).

19. M. C. Wintersgill, J. J. Fontanella, P. Welcher, R. J. Kimble, Jr., and C. G. Andeen, J. Phys. C 13, L661 (1980).

20. J. J. Fontanella, M. C. Wintersgill, A. V. Chadwick, R. Saghafian, and C. G. Andeen, J. Phys. C 14, 2451 (1981).

21. N. E. Hill, W. E. Vaughan, A. H. Price, and M. Davies, Dielectric Properties and Molecular Behavior, (Van Nostrand Reinhold, London, 1969).

22. A. Azimi, V. M. Carr, A. V. Chadwick, F. G. Kirkwood, and R. Saghafian, to be published.

23. R. W. Bonne and J. Schoonman, J. Electrochem. Soc. 124, 28 (1977).

24. V. A. Arkhangel'skaya, V. G. Erofeichev, and M. N. Kiseleva, Sov. Phys. Solid State 14, 2953 (1973).

25. J. Schoonman, G. A. Korteweg, and R. W. Bonne, Solid St. Comm., 16, 9 (1975).

Table 1. Parameters describing the principal relaxation in 0.1 mol% PbF_2:La and PbF_2:Ce.

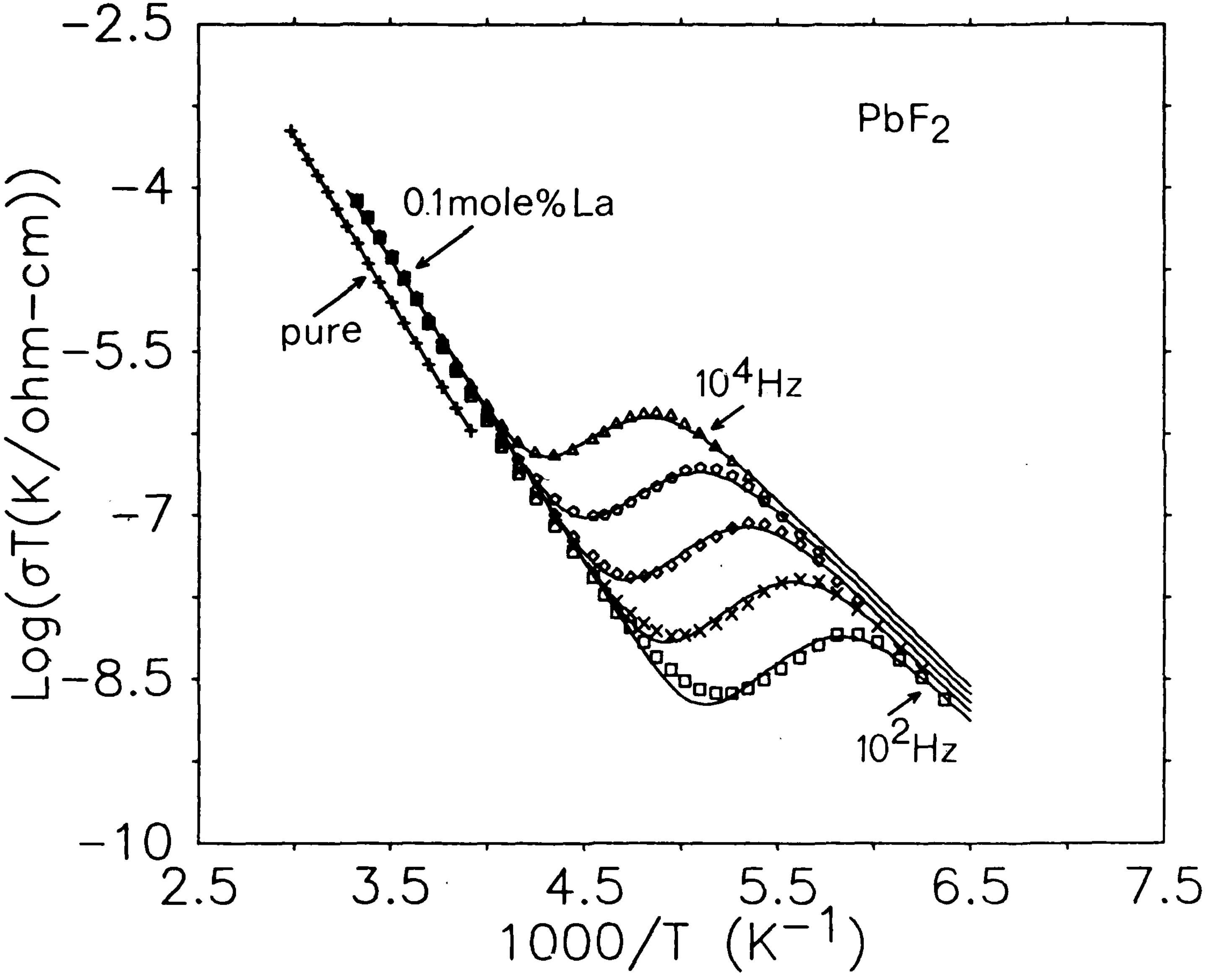
Dopant	A(K)	τ_o(10^{-14}s)	E(eV)	α			$\frac{d\ln\tau}{dP}$(GPa^{-1})	ΔV*(cm^3/mole)
La	364	0.25	0.40	0.14	Sample 1	181K	-1.25	-1.88
						185K	-1.23	-1.89
					Sample 2	181K	-1.17	-1.76
						185K	-1.16	-1.78
Ce	261	1.6	0.32	0.04	Sample 1	161K	-1.34	-1.79

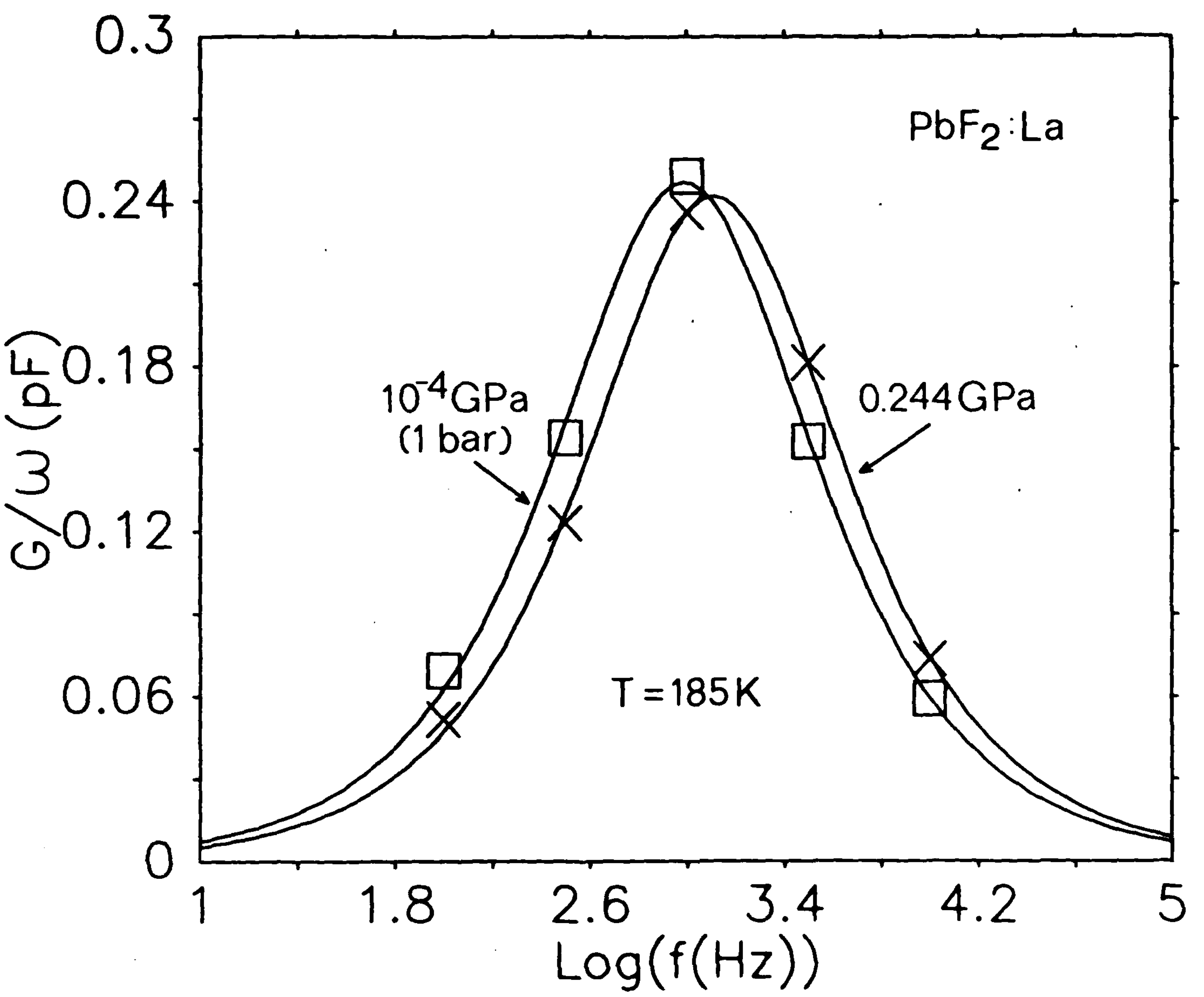
FIGURE CAPTIONS

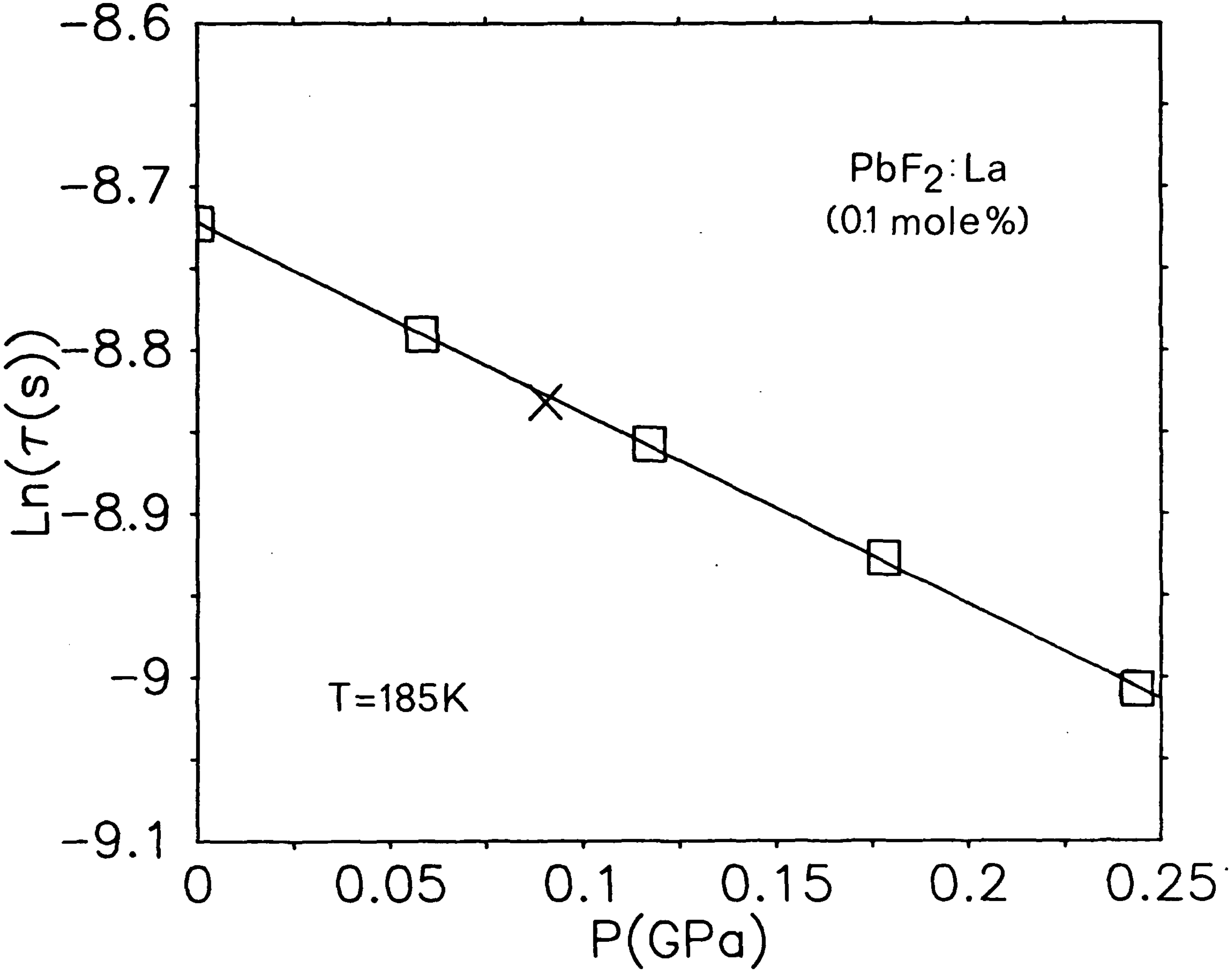
Figure 1. Log(σT(K/ohm-cm)) vs. 1000/T (K^{-1}) for "pure" PbF_2 and 0.1 mol% PbF_2:La. The data for the pure sample is at 100 Hz and the frequencies for PbF_2:La are equal logarithmic intervals between those indicated on the drawing. Also shown is the best fit curve for PbF_2:La.

Figure 2. Log(f(Hz)) vs. G/ω (pF) for 0.1 mol% PbF_2:La at 185K and P=0.0001 GPa (o) and P=0.244 GPa (x). Also shown are the best fit Cole-Cole curves.

Figure 3. Ln(τ(s)) vs. P(GPa) for 0.1 mol% PbF_2:La. Decreasin pressure-o; Increasing pressure-x.


PbF$_2$
0.1mole%La
pure
10^{4}Hz
10^{2}Hz
Log(σT(K/ohm-cm))
−2.5
−4
−5.5
−7
−8.5
−10
2.5
3.5
4.5
5.5
6.5
7.5
1000/T (K^{-1})


0.3
0.24
0.18
0.12
0.06
0
G/ω (pF)
1
1.8
2.6
3.4
4.2
5
Log(f(Hz))
PbF_2:La
10^{-4}GPa
(1 bar)
0.244GPa
T = 185K


PbF_2:La
(0.1 mole%)
T=185K
Ln(τ(s))
-8.6
-8.7
-8.8
-8.9
-9
-9.1
0
0.05
0.1
0.15
0.2
0.25
P(GPa)

DL/413/83/01
GEN/413-2

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 413 800 N. Quincy Street Arlington, Virginia 22217	2
ONR Pasadena Detachment Attn: Dr. R. J. Marcus 1030 East Green Street Pasadena, California 91106	1
Commander. Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Washington, D.C. 20360	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12
DTNSRDC Attn: Dr. G. Bosmajian Applied Chemistry Division Annapolis, Maryland 21401	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1
Naval Ocean Systems Center Attn: Technical Library San Diego, California 92152	1
Naval Weapons Center Attn: Dr. A. B. Amster Chemistry Division China Lake, California 93555	1
Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Dean William Tolles Naval Postgraduate School Monterey, California 93940	1
U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Mr. Vincent Schaper DTNSRDC Code 2830 Annapolis, Maryland 21402	1
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Mr. A. M. Anzalone Administrative Librarian PLASTEC/ARRADCOM Bldg 3401 Dover, New Jersey 07801	1

DL/413/83/01
359/413-2

TECHNICAL REPORT DISTRIBUTION LIST, 359

Dr. Paul Delahay
Department of Chemistry
New York University
New York, New York 10003

Dr. P. J. Hendra
Department of Chemistry
University of Southampton
Southampton SO9 5NH
United Kingdom

Dr. T. Katan
Lockheed Missiles and
Space Co., Inc.
P.O. Box 504
Sunnyvale, California 94088

Dr. D. N. Bennion
Department of Chemical Engineering
Brighma Young University
Provo, Utah 84602

Dr. R. A. Marcus
Department of Chemistry
California Institute of Technology
Pasadena, California 91125

Mr. Joseph McCartney
Code 7121
Naval Ocean Systems Center
San Diego, California 92152

Dr. J. J. Auborn
Bell Laboratories
Murray Hill, New Jersey 07974

Dr. Joseph Singer, Code 302-1
NASA-Lewis
21000 Brookpark Road
Cleveland, Ohio 44135

Dr. P. P. Schmidt
Department of Chemistry
Oakland University
Rochester, Michigan 48063

Dr. H. Richtol
Chemistry Department
Rensselaer Polytechnic Institute
Troy, New York 12181

Dr. E. Yeager
Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106

Dr. C. E. Mueller
The Electrochemistry Branch
Naval Surface Weapons Center
White Oak Laboratory
Silver Spring, Maryland 20910

Dr. Sam Perone
Chemistry & Materials
Science Department
Lawrence Livermore National Lab.
Livermore, California 94550

Dr. Royce W. Murray
Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514

Dr. G. Goodman
Johnson Controls
5757 North Green Bay Avenue
Milwaukee, Wisconsin 53201

Dr. B. Brummer
EIC Incorporated
111 Chapel Street
Newton, Massachusetts 02158

Dr. Adam Heller
Bell Laboratories
Murray Hill, New Jersey 07974

Electrochimica Corporation
Attn: Technical Library
2485 Charleston Road
Mountain View, California 94040

Library
Duracell, Inc.
Burlington, Massachusetts 01803

Dr. A. B. Ellis
Chemistry Department
University of Wisconsin
Madison, Wisconsin 53706

TECHNICAL REPORT DISTRIBUTION LIST, 359

Dr. M. Wrighton
Chemistry Department
Massachusetts Institute
of Technology
Cambridge, Massachusetts 02139

Dr. B. Stanley Pons
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

Donald E. Mains
Naval Weapons Support Center
Electrochemical Power Sources Division
Crane, Indiana 47522

S. Ruby
DOE (STOR)
M.S. 6B025 Forrestal Bldg.
Washington, D.C. 20595

Dr. A. J. Bard
Department of Chemistry
University of Texas
Austin, Texas 78712

Dr. Janet Osteryoung
Department of Chemistry
State University of New York
Buffalo, New York 14214

Dr. Donald W. Ernst
Naval Surface Weapons Center
Code R-33
White Oak Laboratory
Silver Spring, Maryland 20910

Mr. James R. Moden
Naval Underwater Systems Center
Code 3632
Newport, Rhode Island 02840

Dr. Bernard Spielvogel
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709

Dr. William Ayers
ECD Inc.
P.O. Box 5357
North Branch, New Jersey 08876

Dr. M. M. Nicholson
Electronics Research Center
Rockwell International
3370 Miraloma Avenue
Anaheim, California

Dr. Michael J. Weaver
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Dr. R. David Rauh
EIC Corporation
111 Chapel Street
Newton, Massachusetts 02158

Dr. Aaron Wold
Department of Chemistry
Brown University
Providence, Rhode Island 02192

Dr. Martin Fleischmann
Department of Chemistry
University of Southampton
Southampton SO9 5NH ENGLAND

Dr. R. A. Osteryoung
Department of Chemistry
State University of New York
Buffalo, New York 14214

Dr. Denton Elliott
Air Force Office of Scientific
Research
Bolling AFB
Washington, D.C. 20332

Dr. R. Nowak
Naval Research Laboratory
Code 6130
Washington, D.C. 20375

Dr. D. F. Shriver
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

Dr. Aaron Fletcher
Naval Weapons Center
Code 3852
China Lake, California 93555

TECHNICAL REPORT DISTRIBUTION LIST, 359

Dr. David Aikens
Chemistry Department
Rensselaer Polytechnic Institute
Troy, New York 12181

Dr. A. P. B. Lever
Chemistry Department
York University
Downsview, Ontario M3J1P3

Dr. Stanislaw Szpak
Naval Ocean Systems Center
Code 6343, Bayside
San Diego, California 95152

Dr. Gregory Farrington
Department of Materials Science
and Engineering
University of Pennsylvania
Philadelphia, Pennsylvania 19104

M. L. Robertson
Manager, Electrochemical
and Power Sources Division
Naval Weapons Support Center
Crane, Indiana 47522

Dr. T. Marks
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

Dr. Micha Tomkiewicz
Department of Physics
Brooklyn College
Brooklyn, New York 11210

Dr. Lesser Blum
Department of Physics
University of Puerto Rico
Rio Piedras, Puerto Rico 00931

Dr. Joseph Gordon, II
IBM Corporation
K33/281
5600 Cottle Road
San Jose, California 95193

Dr. D. H. Whitmore
Department of Materials Science
Northwestern University
Evanston, Illinois 60201

Dr. Alan Bewick
Department of Chemistry
The University of Southampton
Southampton, SO9 5NH ENGLAND

Dr. E. Anderson
NAVSEA-56Z33 NC #4
2541 Jefferson Davis Highway
Arlington, Virginia 20362

Dr. Bruce Dunn
Department of Engineering &
Applied Science
University of California
Los Angeles, California 90024

Dr. Elton Cairns
Energy & Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Dr. D. Cipris
Allied Corporation
P.O. Box 3000R
Morristown, New Jersey 07960

Dr. M. Philpott
IBM Corporation
5600 Cottle Road
San Jose, California 95193

Dr. Donald Sandstrom
Department of Physics
Washington State University
Pullman, Washington 99164

Dr. Carl Kannewurf
Department of Electrical Engineering
and Computer Science
Northwestern University
Evanston, Illinois 60201

DL/413/83/01
359/413-2

TECHNICAL REPORT DISTRIBUTION LIST, 359

Dr. Robert Somoano
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California 91103

Dr. Johann A. Joebstl
USA Mobility Equipment R&D Command
DRDME-EC
Fort Belvoir, Virginia 22060

Dr. Judith H. Ambrus
NASA Headquarters
M.S. RTS-6
Washington, D.C. 20546

Dr. Albert R. Landgrebe
U.S. Department of Energy
M.S. 6B025 Forrestal Building
Washington, D.C. 20595

Dr. J. J. Brophy
Department of Physics
University of Utah
Salt Lake City, Utah 84112

Dr. Charles Martin
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Dr. H. Tachikawa
Department of Chemistry
Jackson State University
Jackson, Mississippi 39217

Dr. Theodore Beck
Electrochemical Technology Corp.
3935 Leary Way N.W.
Seattle, Washington 98107

Dr. Farrell Lytle
Boeing Engineering and
Construction Engineers
P.O. Box 3707
Seattle, Washington 98124

Dr. Robert Gotscholl
U.S. Department of Energy
MS G-226
Washington, D.C. 20545

Dr. Edward Fletcher
Department of Mechanical Engineering
University of Minnesota
Minneapolis, Minnesota 55455

~~Dr. John Fontanella~~
~~Department of Physics~~
~~U.S. Naval Academy~~
~~Annapolis, Maryland 21402~~

Dr. Martha Greenblatt
Department of Chemistry
Rutgers University
New Brunswick, New Jersey 08903

Dr. John Wasson
Syntheco, Inc.
Rte 6 - Industrial Pike Road
Gastonia, North Carolina 28052

Dr. Walter Roth
Department of Physics
State University of New York
Albany, New York 12222

Dr. Anthony Sammells
Eltron Research Inc.
710 E. Ogden Avenue #108
Naperville, Illinois 60540

Dr. W. M. Risen
Department of Chemistry
Brown University
Providence, Rhode Island 02192

Dr. C. A. Angell
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Dr. Thomas Davis
Polymer Science and Standards
Division
National Bureau of Standards
Washington, D.C. 20234