

ARMY RESEARCH LABORATORY

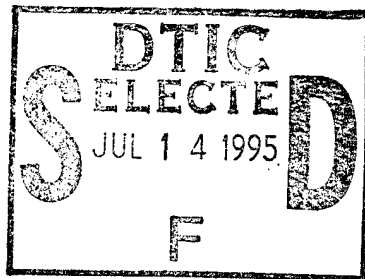


Point-Charge Analysis of Symmetry-  
Preserving Charge Compensation and  
Vacancies in the Fluorapatites  
 $\text{Ca}_5(\text{PO}_4)_3\text{F}$  and  $\text{Sr}_5(\text{PO}_4)_3\text{F}$

by Clyde A. Morrison

ARL-TR-703

June 1995



19950710 114

Approved for public release; distribution unlimited.

DTIC QUALITY INSPECTED 8

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE June 1995		3. REPORT TYPE AND DATES COVERED Interim, October 1993–October 1994
4. TITLE AND SUBTITLE Point-Charge Analysis of Symmetry-Preserving Charge Compensation and Vacancies in the Fluorapatites $\text{Ca}_5(\text{PO}_4)_3$ and $\text{Sr}_5(\text{PO}_4)_3\text{F}$			5. FUNDING NUMBERS DA PR: AH44 PE: 61112A	
6. AUTHOR(S) Clyde A. Morrison				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory Attn: AMSRL-PS-AA 2800 Powder Mill Road Adelphi, MD 20783-1197			8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-703	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory 2800 Powder Mill Road Adelphi, MD 20783-1197			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES AMS code: 611102H4477 ARL PR: 57E771				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) <p>A single point-charge model was used to investigate four types of charge compensation and two types of vacancies for the M2 site in <math>\text{M}_5(\text{PO}_4)_3\text{F}</math> (<math>M = \text{Ca}, \text{Sr}</math>). Two effective charges were chosen for the oxygen in the <math>(\text{PO}_4)^{3-}</math> complex. A set of crystal-field components, <math>A_{nm}</math>, was obtained for each assumed compensation or vacancy, and the crystal-field parameters, <math>B_{nm}</math>, for <math>\text{Nd}^{3+}</math> were calculated for each type. The resulting energy levels for <math>\text{Nd}^{3+}</math> were then calculated and the results for each type compared, showing a rather complicated result for the <math>[(L,S)]</math> multiplets higher in energy than the <math>{}^4F_{3/2}</math> multiplet of <math>\text{Nd}^{3+}</math>. Unsuccessful attempts were made to perform a simple correlation analysis, such as the rotational invariants of the crystal-field parameters and the width of the energy splittings of the <math>{}^4I_j</math> and <math>{}^4F_{3/2}</math> multiplets of <math>\text{Nd}^{3+}</math> for each case considered. A calculation for the M1 site is included, and the energy splittings of the <math>{}^4I_j</math> and <math>{}^4F_{3/2}</math> are shown to be comparable to the energy splittings for the M2 sites.</p>				
14. SUBJECT TERMS Rare earth, fluorapatite, neodymium, charge compensation, vacancies, optical spectra			15. NUMBER OF PAGES 22	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	

# Contents

1. Introduction .....	5
2. Theory .....	6
3. Calculation of Crystal-Field Parameters, $B_{nm}$ , for Various Types of Charge Compensation .....	8
4. Discussion and Conclusion .....	12
Acknowledgments .....	14
References .....	14
Distribution .....	17

## Tables

1. Crystallographic data on $M_5(BO_4)_3F$ ( $M = Ca, Sr; B = P, V$ ) .....	6
2. Even- $n$ crystal-field components, $A_{nm}$ ( $cm^{-1}/\text{\AA}^n$ ), for $M2$ site at $(x, y, 1/4)$ in CPAP and SPAP (no charge compensation) .....	7
3. Crystal-field components for a single $F^-$ ion at $(0, 0, 1/4)$ and total $F^-$ ion contribution to crystal-field components at $Ca2$ site at $(x, y, 1/4)$ in $Ca_5(PO_4)_3F$ (CPAP) .....	8
4. Types of charge compensation .....	9
5. $Nd^{3+}$ crystal-field parameters, $B_{nm}$ ( $cm^{-1}$ ), and rotation invariants, $I_n(B)$ ( $cm^{-1}$ ), for different types of charge compensation in CPAP with $q_O = -1.8$ and $-2$ .....	9
6. $Nd^{3+}$ crystal-field parameters, $B_{nm}$ ( $cm^{-1}$ ), and rotation invariants, $I_n(B)$ ( $cm^{-1}$ ), for different types of charge compensation in SPAP with $q_O = -1.8$ and $-2$ .....	10
7. Total crystal-field splittings, $\Delta E_J$ ( $cm^{-1}$ ), of each $J$ multiplet of $Nd^{3+}$ in CPAP in $C_s$ site with $q_O = -1.8$ and $-2$ .....	11
8. Total crystal-field splittings, $\Delta E_J$ ( $cm^{-1}$ ), of each $J$ multiplet of $Nd^{3+}$ in SPAP in $C_s$ site with $q_O = -1.8$ and $-2$ .....	11
9. $Nd^{3+}$ crystal-field parameters, $B_{nm}$ ( $cm^{-1}$ ), and rotational invariants, $I_n(B)$ ( $cm^{-1}$ ), for $C_3$ ( $M1$ ) site in CPAP and SPAP with $q_O = -1.8$ and $-2$ .....	12
10. Total crystal-field splitting, $\Delta E_J$ ( $cm^{-1}$ ), of each $J$ multiplet of $Nd^{3+}$ in CPAP and SPAP in $C_3$ ( $M1$ ) site with $q_O = -1.8$ and $-2$ .....	12

Accession For	
NTIS    CRA&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-1	

# 1. Introduction

The fluorapatites have received considerable attention recently as hosts for rare-earth ions,  $Ln^{3+}$ , and transition-metal ions in various ionization states [1-5]. In the fluorapatites  $M_5(BO_4)_3F$ , the  $M$  ion can be  $Ca^{2+}$  or  $Sr^{2+}$ , which have ionic radii matching  $Ln^{3+}$ ; lanthanide ions can replace the  $M^{2+}$  ion [6]. (For simplicity, the various fluorapatites  $M_5(BO_4)_3F$  can be referred to as MBAP.) However, the replacement of the  $M^{2+}$  ion by  $Ln^{3+}$  must be accompanied by charge compensation, achieved either by the inclusion of some optically neutral impurity ion, such as  $Na^+$  ( $2Ca^{2+} \rightarrow Na^+ + Ln^{3+}$ ) or  $Si^{4+}$  ( $Ca^{2+} + P^{5+} \rightarrow Si^{4+} + Ln^{3+}$ ), or by vacancy creation ( $3Ca^{2+} \rightarrow 2Ln^{3+} +$  a vacant  $Ca^{2+}$  site). Other more sophisticated forms of charge compensation can be and have been suggested [7-9]. In the analysis reported here, I concentrate on two types of charge compensation, which were proposed by Maximova and coworkers some time ago [6,9]. I also consider the case where the charge compensation is remote and unidentified, and the case where the neodymium ion enters the  $M2$  site and a calcium vacancy occurs at one of the two nearest  $M2$  sites in the crystal.

This report considers the fluorapatites  $Ca_5(PO_4)_3F$  (CPAP) and  $Sr_5(PO_4)_3F$  (SPAP), referred to collectively as MPAP. In these fluorapatites, the crystal belongs to the  $P6_3/m$  (176) space group. The  $M$  ions occupy two sites:  $M1$  in the  $4f$  site with  $C_3$  symmetry and  $M2$  in the  $6h$  site with  $C_s$  symmetry [10]. The latter site,  $M2$ , is the subject here, and I assume that the  $Nd^{3+}$  ions occupy this site, which is the site that is generally assumed to be occupied by the rare-earth ions in the apatite hosts.

Three of the six  $M2$  sites (in the unit cell) of the  $P6_3/m$  space group are (in hexagonal crystal coordinates)  $(x, y, 1/4)$ ,  $(-y, x - y, 1/4)$ , and  $(y - x, -x, 1/4)$ , and the three others are given by  $(x, y, z) \rightarrow (-x, -y, -z)$ ; the crystal-field components are always computed at the  $(x, y, 1/4)$  site. The group  $C_s$  has only one operation, which is a reflection in a plane perpendicular to the principal axis, which, in this particular case, is the  $c$ -axis of the hexagonal crystal; since I am interested only in the symmetry-preserving charge compensators, I restrict my attention to the first set ( $z = 1/4$ ) given above. To preserve the  $C_s$  symmetry, I consider the charge compensator ions occupying the sites with  $z = 1/4$ , and in all cases I take the origin, the location of the  $Ln^{3+}$  ion, at  $(x, y, 1/4)$ . Thus, where we have oxygen compensation, I assume that the fluorine ion at  $(0, 0, 1/4)$  is replaced by an oxygen ion. For sodium compensation, I assume that the calcium ions at either  $(-y, x - y, 1/4)$  or  $(y - x, -x, 1/4)$  are replaced by sodium ions (or any ion with +1 values that might occupy the site). Both these types of charge compensation are discussed in some detail by Maksimova and Sobol' [7]. The detailed x-ray data on MPAP for  $M = Ca$  and  $Sr$  are given in table 1 for the representative ions in each site, and the coordinates (hexagonal) for the equivalent sites of each ion are given in the International Tables [10].

Table 1. Crystallographic data on  $M_5(BO_4)_3F$  ( $M = Ca, Sr; B = P, V$ ).

Hexagonal  $C_{6h}^2$  ( $P6_3/m$ ) 176,  $Z = 2$

Ion	Site	Symmetry	$x$	$y$	$z$	$q^a$
M1	4f	$C_3$	2/3	1/3	$z$	2
M2	6h	$C_s$	$x$	$y$	1/4	2
B	6h	$C_s$	$x$	$y$	1/4	$q_B$
O1	6h	$C_s$	$x$	$y$	1/4	$q_O$
O2	6h	$C_s$	$x$	$y$	1/4	$q_O$
O3	12i	$C_1$	$x$	$y$	$z$	$q_O$
F	2a	$C_{3h}$	0	0	1/4	-1

X-ray data on  $M_5(BO_4)_3F$

M	B	$a$ (Å)	$c$ (Å)	$Z_{M1}$	$X_{M2}$	$Y_{M2}$	$X_B$	$Y_B$	$X_{O1}$	$Y_{O1}$
Ca <sup>b</sup>	P	9.3973	6.872	0.0010	0.00712	0.24827	0.36895	0.3985	0.4849	0.3272
Sr <sup>c</sup>	V	10.0077	7.4342	0.0004	0.24943	0.01059	0.3682	0.3982	0.4706	0.5962
Sr <sup>c</sup>	P	9.7153	7.2810	-0.0002	0.23910	-0.01445	0.3992	0.3685	0.3306	0.4810

M	B	$X_{O2}$	$Y_{O2}$	$X_{O3}$	$Y_{O3}$	$Z_{O3}$
Ca <sup>b</sup>	P	0.4667	0.5875	0.2575	0.3421	0.0705
Sr <sup>c</sup>	V	0.4835	0.3160	0.2498	0.3403	0.0671
Sr <sup>c</sup>	P	0.5356	0.1183	0.3441	0.2612	0.0788

<sup>a</sup>Two values of  $q_O$  have been chosen, -2 and -1.8, with  $q_P = -3 - 4q_O$  in each case.

<sup>b</sup>J. M. Hughes, M. Cameron, and K. D. Crowley, *Structural Variations in Natural F, OH, Cl Apatites*, *Am. Mineral.* 74 (1989), 870.

<sup>c</sup>Private communication, R. E. Peale, University of Central Florida.

## 2. Theory

In all the calculations reported here, the crystal-field Hamiltonian for the  $4f^N$  configuration is given by

$$H_{CEF} = \sum_{n \text{ even}} \sum_{m=-n}^n B_{nm}^* \sum_{i=1}^N C_{nm}(i), \quad (1)$$

where the  $B_{nm}$  are the crystal-field parameters and the  $C_{nm}$  are

$$C_{nm}(i) = \sqrt{4\pi/(2n+1)} Y_{nm}(\theta_i, \varphi_i), \quad (2)$$

with

$$C_{n-m} = (-1)^m C_{nm}^*$$

and the  $Y_{nm}$  are the ordinary spherical harmonics. In  $C_s$  symmetry, the values of  $m$  are restricted by  $n + m = 0, \pm 2, \pm 4$ , with  $|m| \leq n$  and  $n = 2, 4$ , and 6. The parameters entering into the free-ion Hamiltonian are from aqueous solution [11], and their values as well as the details of the computation are given elsewhere [12,13]. The crystal-field splitting is predominantly determined by the  $n$ -even  $B_{nm}$ , and, from the discussion above, the number of

$B_{nm}$  for  $C_s$  symmetry is limited to 14, with  $B_{22}$  real and positive; these properties of  $B_{22}$  are simply achieved by a rotation about the z-axis (c-axis). In the three-parameter crystal-field theory [14], the crystal-field parameters,  $B_{nm}$ , are related to the crystal-field components,  $A_{nm}$ , by

$$B_{nm} = \rho_n A_{nm} \quad (3)$$

where the  $\rho_n$  values represent the effective values of  $\langle r^n \rangle$  for the rare-earth ion. Values of  $\rho_n$  have been tabulated for the entire rare-earth series [12]. The crystal-field components are given by

$$A_{nm} = -e^2 \sum_j q_j C_{nm}(\hat{R}_j) / R_j^{n+1} \quad (4)$$

where  $q_j$  is the effective charge in units of electronic charge on the ion at  $R_j$  [15], and the sum is over all the ions in the solid. Equation (4) has been used to calculate the  $A_{nm}$  for the Ca2 site in CPAP and the Sr2 site in SPAP with the x-ray data reported in table 1. Two values of the oxygen charge have been used:  $q_O = -2$  (for which  $q_{Ca} = 2$  and  $q_P = 5$ ) and  $q_O = -1.8$  (for which  $q_{Ca} = 2$  and  $q_P = -4.2$ ), which in both cases maintain the total charge of the  $PO_4$  molecule at  $-3$  ( $q_P = -3 - 4q_O$ ). The value of  $-1.8$  for the oxygen charge was chosen because this value best fit the experimental value of the point charge  $A_{nm}$  determined experimentally for rare-earth ions in  $Y_3Al_5O_{12}$  (yttrium aluminum garnet—YAG). Table 2 has the results of the calculations of the  $A_{nm}$  for the  $C_s$  sites at  $(x, y, 1/4)$  in CPAP and SPAP with no charge compensation. The  $A_{nm}$  for CPAP given in table 2 should correspond to the conjecture of Maksimova and Sobol' [7] for low concentration of  $Nd^{3+}$  ions.

To calculate the effect of replacing the nearest  $F^-$  site at  $(0, 0, 1/4)$  by an  $O^{2-}$  site, I calculate the  $A_{nm}$  for a negative charge at this site and add these  $A_{nm}$  to the corresponding values given in table 2.

Table 2. Even- $n$  crystal-field components,  $A_{nm}$  ( $cm^{-1}/\text{\AA}^n$ ), for  $M2$  site at  $(x, y, 1/4)$  in CPAP and SPAP (no charge compensation).<sup>a</sup>

$A_{nm}$	CPAP <sup>b</sup>				SPAP <sup>c</sup>			
	$q_O = -1.8$		$q_O = -2$		$q_O = -1.8$		$q_O = -2$	
	Re	Im	Re	Im	Re	Im	Re	Im
$A_{20}$	9481	—	11398	—	6535	—	8081	—
$A_{22}$	-2048	-506.5	-2384	-717.6	527.2	-1664	483.1	-2034
$A_{40}$	2031	—	2012	—	1902	-1911	—	—
$A_{42}$	2829	-1801	3187	-1983	-1815	1053	-2021	1204
$A_{44}$	589.8	-2164	369.5	-2417	1124	-1298	1386	-1251
$A_{60}$	90.85	—	121.2	—	113.2	—	141.5	—
$A_{62}$	-329.9	-284.8	-355.9	-315.5	-3.465	-321.1	-7.119	-349.6
$A_{64}$	156.0	70.42	193.1	79.35	-113.7	-39.64	-135.9	-55.88
$A_{66}$	64.57	-158.4	85.17	-175.0	47.50	179.5	63.08	197.7

<sup>a</sup> $x$  and  $y$  for Ca2 and Sr2 sites are given in table 1.

<sup>b</sup>Smallest Ca2 – F distance = 2.3109 Å, smallest Ca2 – Ca2 distance = 4.0025 Å (two ions).

<sup>c</sup>Smallest Sr2 – F distance = 2.3962 Å, smallest Sr2 – Sr2 distance = 4.1504 Å (two ions).

Consider for a moment CPAP: the nearest  $F^-$  to the Ca2 site is at 2.3109 Å, and the next nearest  $F^-$  ions are at 4.1434 Å; these facts would lead one to surmise that most of the contribution of all the fluorine ions is approximately due to this nearest ion. That this is the case is shown in table 3 for CPAP; if a rough estimate of the effect of the nearest  $F^-$  being replaced by an  $O^{2-}$  ion is needed, one can obtain it by adding in the contribution of all the  $F^-$  ions to the total. That is, simply double the contribution of the  $F^-$  ions to the crystal-field components  $A_{nm}$ . However, I do not make that approximation here but evaluate the crystal-field components for a single negative charge at  $(0, 0, 1/4)$  and add this to the total  $A_{nm}$  for the site at  $(x, y, 1/4)$ .

Table 3. Crystal-field components for a single  $F^-$  ion at  $(0, 0, 1/4)$  and total  $F^-$  ion contribution to crystal-field components at Ca2 site at  $(x, y, 1/4)$  in  $Ca_5(PO_4)_3F$  (CPAP).<sup>a</sup>

$A_{nm}$	Single $F^-$		All $F^-$ ions	
	Re	Im	Re	Im
$A_{11}$	-386	15374	-421	17646
$A_{20}$	-4706	—	-2972	—
$A_{22}$	-5756	-289	-6454	-318
$A_{31}$	44.2	-1763	31.3	-1247
$A_{33}$	171	-2270	179	-2327
$A_{40}$	661	—	644	—
$A_{42}$	696	34.9	604	30.3
$A_{44}$	917	92.3	934	92.9
$A_{51}$	-6.55	261	-6.86	274
$A_{53}$	-21.2	281	-20.3	266
$A_{55}$	-47.3	375	-47.5	375
$A_{60}$	-103	—	-108	—
$A_{62}$	-106	-5.30	-110	-5.54
$A_{64}$	-115	-11.6	-112	-11.4
$A_{66}$	-155	-23.5	-155	-23.5
$A_{71}$	1.05	-41.7	1.06	-42.3
$A_{73}$	3.26	-43.3	3.35	-44.6
$A_{75}$	6.00	-47.6	5.95	-47.2
$A_{77}$	11.4	-64.4	11.4	-64.4

<sup>a</sup>All  $A_{nm}$  values in units of  $cm^{-1}/\text{Å}^n$ .

### 3. Calculation of Crystal-Field Parameters, $B_{nm}$ , for Various Types of Charge Compensation

The types of charge compensation considered are given in table 4, and the labels given in table 4 that identify the type of charge compensation are used hereafter. As an example of the method of obtaining crystal-field parameters for  $Nd^{3+}$ , I give the details of the calculation for the C1 type of charge compensation in table 4. The results given in table 2 are for a crystal where each ion in the solid is in the position given in table 1. Then to account for an  $Na^+$  ion replacing a  $Ca^{2+}$  ion at  $(-y, x - y, 1/4)$ , we can calculate the  $A_{nm}$  for a single charge of  $-1$  at that point and add these  $A_{nm}$  to the appropriate  $A_{nm}$  of table 2. After this, the resulting  $A_{nm}$  are rotated so that

$A_{22}$  is real and positive [16]. Using the rotated  $A_{nm}$ , we can calculate the crystal-field parameters for  $\text{Nd}^{3+}$  by using equation (3). For the D types of table 4, we can create a vacancy at the two  $\text{Ca}^{2+}$  sites by choosing a  $-2$  charge at the D1 or D2 site in the table, and the resulting  $A_{nm}$  are treated as in the C1 case discussed above. The results for all the cases of table 4 are given in tables 5 and 6. The invariants,  $I_n(B)$ , given by [17]

$$I_n(B) = \left[ \sum_{m=-n}^n B_{nm}^* B_{nm} \right]^{1/2}, \quad (5)$$

were calculated and are also given in tables 5 and 6. The results given in tables 5 and 6 show that the crystal-field parameters,  $B_{nm}$ , for the different types of charge compensation vary considerably; except for the B type ( $\text{F}^- \rightarrow \text{O}^{2-}$ ), however, these variations have little effect on the  $I_n(B)$  for the different forms of charge compensation. The result found here for six of the possibly numerous charge compensation possibilities is indicative of the

**Table 4. Types of charge compensation considered in text.<sup>a</sup>**

Type	Remark
A	No charge compensation
B	$\text{Ca}^{2+}$ and $\text{F}^-$ are replaced by $\text{O}^{2-}$ at $(0, 0, 1/4)$ , and $\text{Nd}^{3+}$ at $(x, y, 1/4)$
C1	$\text{Ca}^{2+}$ at $(-y, x - y, 1/4)$ replaced by $\text{Na}^+$
C2	$\text{Ca}^{2+}$ at $(y - x, -x, 1/4)$ replaced by $\text{Na}^+$
D1	$\text{Ca}^{2+}$ at $(-y, x - y, 1/4)$ removed (a charge $-2$ at this site)
D2	$\text{Ca}^{2+}$ at $(y - x, -x, 1/4)$ removed (a charge $-2$ at this site)

<sup>a</sup>Crystal field is calculated for the site at  $(x, y, 1/4)$ , with  $x$  and  $y$  for the Ca2 site given in table 1. In all cases read  $\text{Ca}^{2+}$  as meaning  $\text{Ca}^{2+}$  or  $\text{Sr}^{2+}$ . ( $\text{Na}^+$  can be taken as any possible replacement ion with valence of  $+1$ .)

**Table 5.  $\text{Nd}^{3+}$  crystal-field parameters,  $B_{nm}$  ( $\text{cm}^{-1}$ ), and rotation invariants,  $I_n(B)$  ( $\text{cm}^{-1}$ ), for different types of charge compensation in CPAP with  $q_O = -1.8$  and  $-2$ .<sup>a</sup>**

$B_{nm}$	$q_O = -1.8$						$q_O = -2$					
	A	B	C1	C2	D1	D2	A	B	C1	C2	D1	D2
$B_{20}$	1617	815	1463	1463	1309	1309	1944	1142	1790	1790	1636	1636
$B_{22}$	360	1338	458	505	672	601	425	1399	511	572	642	739
$B_{40}$	1173	1555	1197	1197	1222	1222	1162	1544	1186	1186	1211	1211
$\text{Re}B_{42}$	-1337	-1922	-1795	-907	-611	-1951	-1432	-2087	-1933	-1025	-2141	-778
$\text{Im}B_{42}$	1402	1221	788	1709	1816	360	1627	1392	1032	1908	564	2020
$\text{Re}B_{44}$	-281	611	711	-908	-1106	1152	-593	394	401	-1104	996	-1266
$\text{Im}B_{44}$	-1264	-1348	-1115	-879	-541	-701	-1282	-1483	-1384	-831	-1081	-475
$B_{60}$	144	-19.5	141	141	137	137	193	28.7	189	189	186	186
$\text{Re}B_{62}$	618	735	448	684	699	316	686	791	531	746	393	761
$\text{Im}B_{62}$	314	389	527	128	24.3	616	317	416	537	146	645	44.5
$\text{Re}B_{64}$	272	82.4	201	217	156	92.1	326	146	286	258	175	188
$\text{Im}B_{64}$	-16.5	78.5	188	-165	-225	262	-64.3	74.3	172	-211	288	-277
$\text{Re}B_{66}$	90.7	224	-211	253	274	-274	127	217	-197	281	-308	312
$\text{Im}B_{66}$	256	233	173	104	-13.2	-10.9	282	254	242	133	49.3	14.1
$I_2(B)$	1696	2061	1600	1628	1617	1560	2035	2285	1930	1964	1871	1941
$I_4(B)$	3498	4143	3552	3480	3464	3606	3839	4437	3894	3822	3950	3807
$I_6(B)$	1130	1272	1131	1135	1139	1132	1262	1369	1263	1267	1264	1272

<sup>a</sup>See table 4 for explanation of symbols used for different types of charge compensation.

Table 6. Nd<sup>3+</sup> crystal-field parameters  $B_{nm}$  (cm<sup>-1</sup>), and rotation invariants,  $I_n(B)$  (cm<sup>-1</sup>) for different types of charge compensation in SPAP with  $q_O = -1.8$  and  $-2$ .<sup>a</sup>

$B_{nm}$	$q_O = -1.8$						$q_O = -2$					
	A	B	C1	C2	D1	D2	A	B	C1	C2	D1	D2
$B_{20}$	1115	395	976	976	838	838	1379	659	1240	1240	1102	1102
$B_{22}$	298	1178	422	397	570	533	357	1234	485	443	633	567
$B_{40}$	1099	1417	1119	1119	1139	1139	1104	1422	1124	1124	1144	1144
$\text{Re}B_{42}$	-896	-1299	-602	-1160	-436	-1241	-946	-1404	-672	-1249	-508	-1367
$\text{Im}B_{42}$	-816	-745	-1049	-413	-1127	-160	-975	-857	-1179	-582	-1257	-295
$\text{Re}B_{44}$	-99.2	515	-672	645	-846	932	-390	333	-839	387	-971	813
$\text{Im}B_{44}$	987	1015	693	783	408	457	1005	1120	640	1033	341	781
$B_{60}$	180	52.8	177	177	175	175	225	97.7	222	222	219	220
$\text{Re}B_{62}$	485	600	513	386	507	305	538	644	558	453	554	370
$\text{Im}B_{62}$	-159	-197	4.26	-335	89.7	-410	-139	-204	6.52	-323	88.5	-416
$\text{Re}B_{64}$	184	29.8	177	89.3	140	5.55	233	77.8	209	160	166	65.8
$\text{Im}B_{64}$	-52.6	-91.7	73.8	-172	131	-197	-17.8	-94.6	106	-173	165	-230
$\text{Re}B_{66}$	113	232	289	-218	283	-294	176	243	322	-176	322	-315
$\text{Im}B_{66}$	-273	-276	-60.3	-199	84.2	-18.2	-279	-294	-71.0	-279	72.0	-99.6
$I_2(B)$	1192	1712	1144	1126	1162	1127	1469	1865	1417	1389	1419	1363
$I_4(B)$	2472	2355	2458	2519	2446	2565	2690	3188	2678	2738	2665	2786
$I_6(B)$	895	735	897	896	899	897	997	1115	1000	999	1002	1000

<sup>a</sup>See table 4 for explanation of symbols used for different types of charge compensation.

number of lines that appear in the absorption and emission spectra, as was for example observed by Zounani et al [18] for Eu<sup>3+</sup> in SPAP.

The crystal-field parameters given in tables 5 and 6 were used in calculating the energy levels for Nd<sup>3+</sup>. The details of the procedure used in the calculation are given elsewhere [19]. The calculation covered the lowest 13 multiplets, with a total of 60 energy levels. Instead of presenting all the results, which are quite extensive, I have chosen to give only the width in energy of each multiplet where such a quantity can be reasonably determined. The results for all the  $B_{nm}$  given in tables 5 and 6 are presented in tables 7 and 8. The widths of the  $^4I_J$  ( $J = 9/2$  through  $15/2$ ) and the  $^4F_{3/2}$  are well determined, and greater significance should be given to these multiplets than to the widths of the higher multiplets when one compares these values to experiment. Because of the very large magnitude of the  $B_{nm}$ , in particular  $B_{2m}$ , the higher multiplets are severely mixed. In a number of cases, the mixture was so great that the number of levels of a multiplet allowed by group theory was exceeded. This occurred numerous times for the  $^4S_{3/2}$  levels, which had three levels identified (the levels are identified by the largest coefficient of the state in the wave function for that state), where by group theory there should be only two. This result does not indicate an error in the calculation; it simply means that the crystal field is so strong that in these spectral regions it renders meaningless the method used to identify the energy levels by assignment to particular multiplets in the weak crystal-field limit. Since the crystal-field parameters given in tables 5 and 6 are reasonable approximations to the values that would be obtained by fitting the spectra, these results indicate the difficulties to be expected in the analysis of experimental data.

Table 7. Total crystal-field splittings,  $\Delta E_J$  ( $\text{cm}^{-1}$ ), of each  $J$  multiplet of  $\text{Nd}^{3+}$  in CPAP in  $C_s$  site with  $q_0 = -1.8$  and  $-2$ .<sup>a</sup>

[(L,S)J]	$q_0 = -1.8$						$q_0 = -2$					
	A	B	C1	C2	D1	D2	A	B	C1	C2	D1	D2
$^4I_{9/2}$	649	747	632	645	645	624	732	795	714	729	702	729
$^4I_{11/2}$	506	608	482	504	503	460	581	632	557	578	535	577
$^4I_{13/2}$	589	714	564	586	584	542	676	746	652	673	630	671
$^4I_{15/2}$	849	994	823	850	849	800	980	1071	955	980	931	981
$^4F_{3/2}$	228	394	235	238	258	254	262	439	270	276	289	298
$^4S_{3/2}^b$	29	66	32	32	37	38	32	70	37	35	42	40
$^4F_{9/2}$	449	584	440	450	459	458	513	638	500	515	517	525
$^2H_{11/2}$	114	147	105	109	107	103	136	150	125	130	119	127
$^2G_{7/2}^c$	306	402	319	300	294	331	344	431	359	336	373	329

<sup>a</sup>The  $^4F_{5/2}$ ,  $^2H_{9/2}$ , and  $^4F_{7/2}$  are intermixed, as are  $^4G_{5/2}$  and  $^2G_{7/2}$ .

<sup>b</sup>The  $^4S_{3/2}$  multiplet is very strongly mixed with the  $^4F_{7/2}$  multiplet.

<sup>c</sup>The  $^2G_{7/2}$  multiplet is strongly mixed with the  $^4G_{5/2}$  multiplet, and levels belonging to  $^2G_{7/2}$  were arbitrarily selected.

Table 8. Total crystal-field splittings,  $\Delta E_J$  ( $\text{cm}^{-1}$ ), of each  $J$  multiplet of  $\text{Nd}^{3+}$  in SPAP in  $C_s$  site with  $q_0 = -1.8$  and  $-2$ .<sup>a</sup>

[(L,S)J]	$q_0 = -1.8$						$q_0 = -2$					
	A	B	C1	C2	D1	D2	A	B	C1	C2	D1	D2
$^4I_{9/2}$	464	586	461	451	462	449	527	619	525	512	526	505
$^4I_{11/2}$	362	493	360	340	360	321	422	511	420	400	420	381
$^4I_{13/2}$	427	580	424	405	424	385	497	605	495	475	493	455
$^4I_{15/2}$	623	807	623	600	624	580	727	1859	727	705	727	683
$^4F_{3/2}$	173	309	178	178	192	195	207	347	215	211	231	226
$^4S_{3/2}^b$	36	49	36	37	26	27	28	53	29	30	30	33
$^4F_{9/2}$	314	457	318	317	332	336	364	495	367	362	380	378
$^2H_{11/2}$	81	125	78	77	77	79	96	128	93	90	92	90
$^2G_{7/2}^c$	235	369	234	246	234	258	229	393	228	265	228	250

<sup>a</sup>The  $^4F_{5/2}$ ,  $^2H_{9/2}$ , and  $^4F_{7/2}$  are intermixed, as are  $^4G_{5/2}$  and  $^2G_{7/2}$ .

<sup>b</sup>The  $^4S_{3/2}$  multiplet is very strongly mixed with the  $^4F_{7/2}$  multiplet.

<sup>c</sup>The  $^2G_{7/2}$  multiplet is strongly mixed with the  $^4G_{5/2}$  multiplet, and levels belonging to  $^2G_{7/2}$  were arbitrarily selected.

As a final computation, the crystal-field components,  $A_{nm}$ , were calculated for the M1 site with  $C_3$  symmetry in CPAP and SPAP, and the crystal-field parameters were calculated for  $\text{Nd}^{3+}$ . In these calculations, charge compensation was ignored. The results for both CPAP and SPAP are given in table 9 along with the invariants  $I_n(B)$  for each case. This calculation corresponds to type A in table 4 for the M2 site. On comparing  $I_n(B)$  from table 5 for type A with the  $I_n(B)$  of table 9 for CPAP, we find that  $I_2(B)$  and  $I_4(B)$  for  $C_s$  symmetry are larger than  $I_2(B)$  and  $I_4(B)$  for  $C_3$  symmetry. However, the opposite is true for the corresponding values of  $I_6(B)$ , where  $I_6(B)$  for the M1 site in CPAP is larger than  $I_6(B)$  for the M2 site in CPAP. This same result is true for the  $I_n(B)$  in SPAP. The energy widths of the multiplets are given in table 10, and a comparison of the results for case A in table 7 shows mixed results; that is, some of the widths of the multiplets for the

Table 9. Nd<sup>3+</sup> crystal-field parameters,  $B_{nm}$  (cm<sup>-1</sup>), and rotational invariants,  $I_n(B)$  (cm<sup>-1</sup>), for C<sub>3</sub> (M1) site in CPAP and SPAP with  $q_O = -1.8$  and  $-2$ .

$B_{nm}, I_n(B)$	CPAP		SPAP	
	$q_O = -1.8$	$q_O = -2$	$q_O = -1.8$	$q_O = -2$
$B_{20}$	1247	1556	936	1173
$B_{40}$	-2252	-2359	-1585	-1646
$B_{43}$	1016	1114	700	759
$B_{60}$	-1176	-1312	-814	-909
$\text{Re}B_{63}$	890	935	629	673
$\text{Im}B_{63}$	-260	-432	65.7	194
$\text{Re}B_{66}$	-117	-3.61	-130	-35.9
$\text{Im}B_{66}$	356	417	-249	-311
$I_2(B)$	1247	1556	936	1173
$I_4(B)$	2671	2837	1869	1965
$I_6(B)$	1544	2047	1064	1415

Table 10. Total crystal-field splitting,  $\Delta E_J$  (cm<sup>-1</sup>), of each  $J$  multiplet of Nd<sup>3+</sup> in CPAP and SPAP in C<sub>3</sub> (M1) site with  $q_O = -1.8$  and  $-2$ .

$[(L,S)]$	CPAP		SPAP	
	$q_O = -1.8$	$q_O = -2$	$q_O = -1.8$	$q_O = -2$
$^4I_{9/2}$	667	735	471	529
$^4I_{11/2}$	373	426	260	298
$^4I_{13/2}$	439	4892	308	347
$^4I_{15/2}$	861	944	595	652
$^4F_{3/2}$	144	167	117	139
$^4S_{3/2}$	26	30	17	21
$^4F_{9/2}$	367	422	268	308
$^2H_{11/2}$	142	165	98	114
$^2G_{7/2}$	324	362	233	255

M1 sites in table 10 are larger than the corresponding multiplets for the M2 sites given in table 7. The results for SPAP given in table 10 and for case A of table 8 are similar to the result for CPAP.

## 4. Discussion and Conclusion

A number of the calculations presented here were made in an attempt to find some general trend and eventually a simple criterion that could be used to sort out the various sites in the experimental data. The rotational invariants are one such quantity that I chose in the attempt to correlate the  $I_n(B)$  with the  $\Delta E_J$  of various multiplets. In particular, if we select the  $^4F_{3/2}$  splittings and compare them with the  $I_2(B)$  for the different charge compensations, the results for the splittings  $\Delta E$  ( $^4F_{3/2}$ ) are  $B > D1 > D2 > C2 > C1 > A$ ; for  $I_2(B)$ , on the other hand,  $B > A > C2 > D1 > C1 > D2$ . If the crystal field were weaker, one would expect a one-to-one correlation between  $I_2(B)$  and  $\Delta E$  ( $^4F_{3/2}$ ), since for weak crystal fields,  $\Delta E$  ( $^4F_{3/2}$ ) must be proportional to  $I_2(B)$  when  $J$ -mixing by the crystal field is ignored. However, that  $J$ -mixing cannot be ignored is obvious from the above results. An examination of the composition of the  $^4F_{3/2}$  eigenfunctions reveals that the  $^4F_{3/2}$  lowest energy level wavefunction for case B in CPAP ( $q_O = -2$ ) is approximately

$$90\% {}^4F_{3/2} + 6\% {}^4F_{5/2} + 1\% {}^4G_{5/2};$$

for the same case, the highest level for the  ${}^4F_{3/2}$  eigenfunction is

$$91\% {}^4F_{3/2} + 3\% {}^4F_{5/2} + 3\% {}^4F_{7/2}.$$

For case A, the wavefunctions for the corresponding levels are

$$95\% {}^4F_{3/2} + 3\% {}^4F_{5/2} + 0.50\% {}^4F_{7/2}$$

for the lowest energy, and

$$92\% {}^4F_{3/2} + 5\% {}^4F_{5/2} + 1\% {}^4F_{7/2}$$

for the highest. This admixture of the wavefunctions of different  $J$  values, caused by the strength of the crystal field, makes a simple first analysis of the experimental observation of the splitting of the  ${}^4F_{3/2}$  impossible. Obviously, for the higher energy multiplets, which are not so well isolated from one another, the mixing is confusingly severe: For case A in CPAP ( $q_O = -2$ ), the wavefunction for the lower  ${}^4S_{3/2}$  is

$$71\% {}^4S_{3/2} + 24\% {}^4F_{7/2} + 2\% {}^4F_{5/2}$$

and for the highest is

$$83\% {}^4S_{3/2} + 15\% {}^4F_{7/2} + 1\% {}^4F_{9/2}.$$

Thus, the operator equivalent method or any other method that ignores  $J$ -mixing by the crystal field would fall far short of the mark of a good representation of the experimental situation.

The relationship of the  ${}^4I_J \Delta E_J$  to the  $I_n(B)$  is quite complicated even in theory, and one might analyze a direct relation to the  $B_{nm}$  themselves by using some of the results given by Karayianis [20] where  $J$ -mixing by the crystal field is included.

Finally, a calculation of the crystal-field parameters for  $\text{Nd}^{3+}$  in the  $M1$  site (table 1) with  $C_3$  symmetry for  $q_O = -1.8$  and  $-2$  was performed for the case of no charge compensation; these results are given in table 9 for CPAP and SPAP. This calculation corresponds to the A type of calculation of table 4. The  $I_n(B)$  values in comparison with the corresponding values of  $I_n(B)$  for the  $M1$  in table 9 show that  $I_2(B)$  and  $I_4(B)$  are larger for the  $M2$  site than for the  $M1$  site, but the reverse is true for the corresponding values of  $I_6(B)$ . However, the  $\Delta E_J$  for the different multiplets of the  ${}^4I$  term show erratic behavior; that is, for the  $q_O = -1.8$  in CPAP, the  $\Delta E_{9/2}$  for  $M2$  are smaller than those for  $M1$ ; for  $\Delta E_{11/2}$ ,  $M2 > M1$ ; for  $\Delta E_{13/2}$ ,  $M2 > M1$ ; for  $\Delta E_{15/2}$ ,  $M2 < M1$ . Similar results are obtained for SPAP. Thus it is apparently not possible to separate the experimental data by sites by identifying the width of the splitting of even well-defined multiplets ( ${}^4I_J$ ), unless a careful analysis of these splittings using some of the results of Karayianis [20] revealed a somewhat simple relationship of these splittings of the multiplets with the crystal-field parameters.

## Acknowledgments

I have received much encouragement and technical assistance in this work from my coworkers, Donald Wortman, John Bruno, and Richard Leavitt. Also, I wish to thank John Gruber of San Jose State University for long and tedious discussions on the problem of charge compensation, which at times included Bruce Chai of the Center for Research and Education in Optics and Lasers (CREOL). I have also benefited from discussions with Michael Seltzer and Andrew Wright of the Naval Air Warfare Center Weapons Division at China Lake. Included also in discussions of the "apatite problem" are J. Andrew Hutchinson of Night Vision, Bahram Zandi and Larry Merkle of Army Research Laboratory at Ft. Belvoir, and Toomas Allik of SAIC. Suggestions have also been received from Robert Peale of the University of Central Florida. To all of these, I wish to say thanks for your advice.

## References

1. P. Hong, X. X. Zhang, G. Loutts, R. E. Peale, H. Weidner, B. Chai, S. A. Payne, L. D. DeLoach, L. K. Smith, and W. F. Krupke, *Lasing and Spectroscopic Characteristics of a New Nd Laser Crystal—Strontium Fluorovanadate*, Advanced Solid-State Lasers Topical Meeting, Salt Lake City, 7–10 February 1994, paper ATuB2.
2. L. D. DeLoach, S. A. Payne, L. K. Smith, W. F. Krupke, B.H.T. Chai, and G. Loutts, *New Yb-Doped Apatite Crystals for Flexible Laser Design*, Advanced Solid-State Lasers Topical Meeting, Salt Lake City, 7–10 February 1994, paper ATuB3.
3. L. D. Merkle, B. Zandi, H. R. Verdun, B. McIntosh, B.H.T. Chai, J. B. Gruber, M. D. Seltzer, and C. A. Morrison, *Spectroscopic Study of Pr:Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F and Pr:SrAl<sub>12</sub>O<sub>19</sub> as Potential Visible Laser Materials*, Advanced Solid-State Lasers Topical Meeting, Salt Lake City, 7–10 February 1994, paper ATuC2.
4. R. E. Peale, P. L. Summers, H. Weidner, P. Hong, and B.H.T. Chai, *Site Selective Nd<sup>3+</sup> Photoluminescence in Strontium Fluorovanadate*, Advanced Solid-State Lasers Topical Meeting, Salt Lake City, 7–10 February 1994, paper AWB6.
5. B. Chai, G. Loutts, X. X. Zhang, P. Hong, M. Bass, I. A. Shcherbakov, and A. I. Zagumennyi, *Comparison of Laser Performance of Nd Doped YVO<sub>4</sub>, GdVO<sub>4</sub>, and Sr<sub>5</sub>(VO<sub>4</sub>)<sub>3</sub>F*, Advanced Solid-State Lasers Topical Meeting, Salt Lake City, 7–10 February 1994, paper AWC1.
6. D. A. Grisafe and F. A. Hummel, *Pentavalent Ion Substitutions in the Apatite Structure; Part A. Crystal Chemistry*, *J. Solid State Chem.* **2** (1970), 160.

7. G. V. Maksimova and A. A. Sobol', *Local Charge Compensation of the Nd<sup>3+</sup> Ion in Fluorapatite Crystals*, *Inorg. Mater.* **8** (1972), 945 [Trans. Neorg. Mater. **8** (1972), 1077] and G. V. Maksimova and A. A. Sobol', *Tr. Fiz. Inst. Akad. Nauk* **60** (1972), 55.
8. A. G. Avanesov, T. T. Basiev, Yu. K. Voron'ko, B. I. Denker, G. V. Maksimova, V. A. Myzina, V. V. Osiko, and V. S. Fedorov, *Investigation of Spatial Distribution of Impurities in Solids by the Method of Kinetic Luminescent Spectroscopy*, *Sov. Phys. JETP* **57** (1983), 596. [Trans. Zh. Eksp. Teor. Fiz. **84** (1983), 1028].
9. G. V. Maksimova and A. A. Sobol', *Nd<sup>3+</sup> Optical Centers in Crystals of Calcium and Strontium Fluorophosphates*, *Tr. Fiz. Inst. Akad. Nauk* **60** (1972), 55.
10. N.F.M. Henry and K. Lonsdale, *International Tables for X-Ray Crystallography, Vol. I: Symmetry Groups*, Kynoch, Birmingham, U.K. (1969).
11. W. T. Carnall, P. R. Fields, and K. Rajnak, *Spectral Intensities of the Trivalent Lanthanides and Actinides in Solution. II. Pm<sup>3+</sup>, Sm<sup>3+</sup>, Eu<sup>3+</sup>, Gd<sup>3+</sup>, Tb<sup>3+</sup>, Dy<sup>3+</sup>, and Ho<sup>3+</sup>*, *J. Chem. Phys.* **49** (1968), 4412. *Electronic Energy Levels in the Trivalent Lanthanide Aquo Ions. I. Pr<sup>3+</sup>, Nd<sup>3+</sup>, Pm<sup>3+</sup>, Sm<sup>3+</sup>, Dy<sup>3+</sup>, Ho<sup>3+</sup>, Er<sup>3+</sup>, and Tm<sup>3+</sup>*, *J. Chem. Phys.* **49** (1968), 4424; *Electronic Energy Levels of the Trivalent Lanthanide Aquo Ions. II. Gd<sup>3+</sup>*, *J. Chem. Phys.* **49** (1968), 4443; *Electronic Energy Levels of the Trivalent Lanthanide Aquo Ions. III. Tb<sup>3+</sup>*, *J. Chem. Phys.* **49** (1968), 4447; *Electronic Energy Levels of the Trivalent Lanthanide Aquo Ions. IV. Eu<sup>3+</sup>*, *J. Chem. Phys.* **49** (1968), 4450.
12. C. A. Morrison and R. P. Leavitt, *Crystal Field Analysis of Triply Ionized Rare Earth Ions in Lanthanum Trifluoride*, *J. Chem. Phys.* **71** (1979), 2366.
13. C. A. Morrison and R. P. Leavitt, "Spectroscopic Properties of Triply Ionized Lanthanides in Transparent Host Crystals," in *Handbook of the Physics and Chemistry of Rare Earths*, Vol. 5, K. Gschneidner and L. Eyring, eds., North-Holland, New York (1982).
14. R. P. Leavitt, C. A. Morrison, and D. E. Wortman, *Rare-Earth Ion-Host Interactions 3. Three Parameter Theory of Crystal Fields*, Harry Diamond Laboratories, HDL-TR-1673 (June 1975), NTIS AD A017 849.
15. N. Karayianis and C. A. Morrison, *Rare-Earth Ion-Host Interactions 1. Point Charge Lattice Sum in Scheelites*, Harry Diamond Laboratories, HDL-TR-1648 (October 1973), NTIS AD 776 330.
16. C. A. Morrison, *Angular Momentum Theory Applied to Interactions in Solids*, *Lecture Notes in Chemistry*, **47**, Springer-Verlag, New York (1988), pp 86, 87.
17. C. A. Morrison, *Crystal Fields for Transition-Metal Ions in Laser Host Materials*, Springer-Verlag, New York (1992), p 9.

18. Z. Zounani, D. Xambon, and J. C. Cousseins, *Optical Properties of  $\text{Eu}^{3+}$  Activated  $\text{Sr}_{10}\text{F}_2(\text{PO}_4)_6$  Elaborated by Coprecipitation*, *J. Alloys Compounds* **188** (1992), 82.
19. C. A. Morrison and D. E. Wortman, "Energy Levels, Transition Probabilities, and Branching Ratios for Rare-Earth Ions in Transparent Solids," in *Novel Laser Sources and Applications*, J. F. Becker, A. C. Tarn, J. B. Gruber, and L. Lasen, eds., SPIE Optical Engineering Press (1994), pp 67–85.
20. N. Karayianis, *The Significance of Crystal-Field Parameters for the  $^4I$  Term of  $\text{Nd}^{3+}$  in  $\text{CaWO}_4$* , Harry Diamond Laboratories, HDL-TR-1674 (December 1974), NTIS AD A011 251.

## Distribution

Admnstr  
Defns Techl Info Ctr  
Attn DTIC-DDA (2 copies)  
Cameron Sta Bldg 5  
Alexandria VA 22304-6145

Director  
Defns Nuc Agcy  
Attn TITL Tech Lib  
6801 Telegraph Rd  
Alexandria VA 22310-3398

Ofc of the Dpty Chief of Staf for  
Rsrch Dev & Acqstn  
Attn DAMA-ARZ-B I R Hershner  
Depart of the Army  
Washington DC 20310

Under Secy of Defns Rsrch & Engrg  
Attn Techl Lib 3C128  
Washington DC 20301

Commander  
Atmospheric Sci Lab  
Attn Techl Lib  
White Sands Missile Range NM 88002-5030

Director  
Night Vsn & Electro-Optics Lab LABCOM  
Attn A Pinto (2 copies)  
Attn B Zandi  
Attn J Daunt  
Attn L Merkel  
Attn R Buser  
Attn J A Hutchinson  
Attn Techl Lib  
Attn W Tressel  
FT Belvoir VA 22060

Commander  
US Army Mis & Munitions Ctr & Schl  
Attn AMSMI-TB Redstone Sci Info Ctr  
Attn ATSK-CTD-F  
Redstone Arsenal AL 35809

US Army Mtrl & Mech Rsrch Ctr  
Attn SLCMT-TL Techl Lib  
Watertown MA 02172

US Army Rsrch Ofc  
Attn G Iafrate  
Attn M Strosio  
Attn M Ciftan  
Attn R Guenther  
PO Box 12211  
Research Triangle Park NJ 07709-2211

US Army Test & Eval Cmnd  
Attn D H Sliney  
Attn Techl Lib  
Aberdeen Proving Ground MD 21005

US Army Troop Spprt Cmnd  
Attn STRNC-RTL Techl Lib  
Natick MA 01762

Commanding Officer  
US Frgn Sci & Techlgy Ctr  
Attn AIAST-BS Basic Sci Div  
Federal Office Building  
Charlottesville VA 22901

Director  
Nav Rsrch Lab  
Attn A Rosenbaum  
Attn Code 2620 Tech Lib Br  
Attn Code 5554 F Bartoli  
Attn Code 5554 L Esterowitz  
Attn Code 5554 R E Allen  
Attn G Risenblatt  
Washington DC 20375

Nav Weapons Ctr  
Attn D C Harris  
Attn M D Seltzer  
Attn Code 3854 M Nader  
Attn Code 3854 R L Atkins  
Attn DOCE343 Techl Info Dept  
China Lake CA 93555

## Distribution

Ames Lab Dow Iowa State Univ  
Attn K A Gschneidner Jr  
Ames IA 50011

Argonne Natl Lab  
Attn W T Carnall  
9700 South Cass Ave  
Argonne IL 60439

Director  
Lawrence Radiation Lab  
Attn M J Weber  
Attn L D DeLoach  
Attn S A Payne  
Attn W Krupke  
Livermore CA 94550

Oak Ridge Natl Lab  
Attn R G Haire  
Oak Ridge TN 37839

NASA Langley Rsrch Ctr  
Attn C Blair  
Attn D Getteny  
Attn G Armagen  
Attn J Barnes (2 copies)  
Attn M Buoncristiani  
Attn N P Barnes  
Attn P Cross  
Hampton VA 23665

Natl Inst of Stand & Technlgy  
Attn Lib  
Gaithersburg MD 20899

Natl Oceanic & Atmospheric Adm Envir  
Rsrch Lab  
Attn Lib R-51 Technl Rpt  
Boulder CO 80302

Arizona State Univ Dept of Chemistry  
Attn L Eyring  
Tempe AZ 85281

Colorado State Univ Physics Dept  
Attn S Kern  
FT Collins CO 80523

Departamento De Química Fundamental &  
Departamento de Fisica  
Attn A da Gama  
Attn G F de Sá  
Attn O L Malta  
da UFPE Cidade Universitaria  
50,000 Recife Pe  
Brasil

Howard Univ Dept of Physics  
Attn Prof V Kushamaha  
25 Bryant Stret NW  
Washington DC 20059

Johns Hopkins Univ Dept of Physics  
Attn B R Judd  
Baltimore MD 21218

MA Inst of Technlgy Crystal Physics Lab  
Attn H P Jenssen  
Cambridge MA 02139

Princeton Univ Dept of Chemistry  
Attn D S McClure  
Attn C Weaver  
Princeton NJ 08544

San Jose State Univ Dept of Physics  
Attn J B Gruber  
San Jose CA 95192

Univ of Central Florida Dept of Physics  
Attn B H T Chai  
Attn R E Peale  
Orlando FL 32816

Univ of Connecticut Dept of Physics  
Attn R H Bartram  
Storrs CT 06269

Univ of Dayton Dept of Physics  
Attn S P Sinha  
300 College Park  
Dayton OH 45469-2350

## Distribution

Univ of Illinois Everitt Lab  
Attn J G Eden  
1406 W Green Stret  
Urbana IL 61801

Univ of Michigan Dept of Physics  
Attn S C Rand  
Ann Arbor MI 48109

Univ of Minnesota Duluth Dept of Chemistry  
Attn L C Thompson  
Duluth MN 55812

Univ of South Florida Physics Dept  
Attn R Chang  
Attn Sengupta  
Tampa FL 33620

Univ of Southern California  
Attn M Birnbaum  
Los Angeles CA 90089

Univ of Virginia Dept of Chemistry  
Attn F S Richardson  
Charlottesville VA 22901

Univ of Wisconsin Chemistry Dept  
Attn J Wright  
Madison WI 53706

UPR 210 CNRS  
Attn M Faucher  
Attn P Caro  
Attn P Porcher  
1 Place A Briand 92195  
Meudon Cedex  
France

Allied Signal Inc  
Attn R Morris  
POB 1021 R  
Morristown NJ 07960

Battelle Pac Northwest Lab Battelle Blvd  
Attn N Hess  
PO Box 999  
Richland WA 99352

Dept of Mech Indus & Arspc Eng  
Attn S Temkin  
PO Box 909  
Piscataway NJ 08854

Engrg Societies Lib  
Attn Acqstn Depart  
345 East 47th Stret  
New York NY 10017

Fibertech Inc  
Attn H R Verdin  
510-A Herdon Pky  
Herdon VA 22070

Hughes Aircraft Comp  
Attn D Sumida  
3011 Malibu Canyon Rd  
Malibu CA 90265

IBM Rsrch Div Almaden Rsrch Ctr  
Attn R M Macfarlane Mail Stop K32 802(d)  
650 Harry Rd  
San Jose CA 95120

Inst for Low Temp & Struc Rsrch Polish  
Academy of Sci  
Attn R Troc  
50-950 Wroclaw PO Box 937  
ul. Okolna 2  
Poland

Lawrence Berkeley Lab  
Attn N Edelstein  
MS 70A-1150  
Berkeley CA 94720

Martin Marietta  
Attn F Crowne  
Attn J Little  
Attn P Caldwell  
Attn T Worchesky  
1450 South Rolling Rd  
Baltimore MD 21227

## Distribution

MIT Lincoln Lab  
Attn B Aull  
PO Box 73  
Lexington MA 02173

Montana Analytic Services  
Attn M Schwan  
325 Icepond Rd  
Bozeman MT 59715

Sci Applctn Intrntl Corp  
Attn T Allik  
1710 Goodridge Dr  
McLean VA 22102

Southwest Rsrch Inst  
Attn M J Sablik  
PO Drawer 28510  
San Antonio TX 78228-0510

Swartz Electro-Optic Inc  
Attn G A Rines  
45 Winthrop Stret  
Concord MA 01742

Union Carbide Corp  
Attn M R Kokta  
50 South 32nd Stret  
Washougal WA 98671

Univ of Toronto Dept of Physics  
Attn D May  
Toronto Ontario MSS1A7  
Canada

W J Schafer Assoc  
Attn J W Collins  
321 Ballerica Rd  
Chelmsford MA 01824

US Army Rsrch Lab  
Attn AMSRL-EP C Thornton  
Attn AMSRL-EP M Thompsett  
Attn AMSRL-EP-C T Aucoin  
FT Monmouth NJ 07703-5601

US Army Rsrch Lab  
Attn AMSRL-OP-SD-TA Mail & Records  
Mgmt

Attn AMSRL-OP-SD-TL Tech Library  
(3 copies)

Attn AMSRL-OP-SD-TP Tech Pub  
Attn AMSRL-PS-AA C Morrison  
(10 copies)

Attn AMSRL-PS-AA D Wortman  
(10 copies)

Attn AMSRL-PS-AA G Simonis  
Attn AMSRL-PS-AA J Bradshaw

Attn AMSRL-PS-AA J Bruno

Attn AMSRL-PS-AA J Pham

Attn AMSRL-PS-AA M Stead

Attn AMSRL-PS-AA M Tobin

Attn AMSRL-PS-AA R Leavitt

Attn AMSRL-PS-AA R Tober

Attn AMSRL-PS-AA T Bahder

Attn AMSRL-SE-EO C Garvin

Attn AMSRL-SE-EO J Goff

Attn AMSRL-SE-EP J Nemarich

Attn AMSRL-SE-RM (A) Chf

Attn AMSRL-SE-RM J Nemarich

Attn AMSRL-SE-RU A Bencivenga

Attn AMSRL-SE-RU B Zabłudowski

Attn AMSRL-SS-FA G Turner

Attn AMSRL-WT Chf Scntst

Attn AMSRL-WT-NG B McLean

Attn AMSRL-WT-NG Chf

Adelphi, MD 20783-1197