CRYSTAL FIELD SPLITTINGS OF THE HUND GROUND STATES OF NAN IONS IN S4 SYMM. (U) HARRY DIAMOND LABS ADELPHI MD C A MORRISON ET AL. MAR 84 HDL-TR-2040
Crystal-Field Splittings of the Hund Ground States of nd\textsuperscript{N} ions in S\textsubscript{4} Symmetry: Theory and Application to the Ga\textsuperscript{3+} Site of Gd\textsubscript{3}Sc\textsubscript{2}Ga\textsubscript{3}O\textsubscript{12}

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**Title**: Crystal-Field Splittings of the Hund Ground States of ndN Ions in S4 Symmetry: Theory and Application to the Ga^3+ Site of Gd_3Sc_2Ga_3O_{12}

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**Abstract**: We discuss the use of the weak-field approximation and the point-charge model to calculate the splittings of the Hund ground states of ndN^+ ions (1 ≤ N ≤ 9) in S4 symmetry. The host crystal chosen as an illustration is Gd_3Sc_2Ga_3O_{12} (gadolinium scandium gallium garnet—GSGG). In this crystal, the ndN^+ ions enter the Gd^3+ sites substitutionally. Lattice sums, A_{nm}, are reported for the Gd^3+ site, and crystal-field parameters, B_{nm}, and energy levels are given for 29 ions with N = 1 to 9. The results of the calculations are discussed for each ion considered.
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1. INTRODUCTION

The purpose of this report is to investigate the crystal-field splittings of the lowest level (the Hund ground state) of the configuration \( n^N (n = 3, 4, 5 \) and \( 1 \leq N \leq 9 \) in \( S_4 \) symmetry. The particular single-crystal material considered as an illustration of our methods is \( \text{Gd}_3\text{Sc}_2\text{Ga}_3\text{O}_{12} \) (gadolinium scandium gallium garnet--GSGG), in which the \( \text{Ga}^{3+} \) ion site has \( S_4 \) symmetry. The material GSGG has recently been shown to be an efficient laser host when doped substitutionally with \( \text{Nd}^{3+} \) (in the \( \text{Gd} \) site) and \( \text{Cr}^{3+} \) (in the Ga site). The high efficiency of this host crystal is due to broad-band absorption by chromium ions and to the efficient transfer of energy from \( \text{Cr}^{3+} \) ions to excited states of \( \text{Nd}^{3+} \) ions (\( ^4\text{F}_{3/2} \) and higher). The absorption bands of \( \text{Cr}^{3+} \) are much broader than those of \( \text{Nd}^{3+} \) so that more energy is extracted from the pump.

The theory presented here is an extension of previous work we have done on rare-earth ions. The present calculations represent a zeroth-order approximation, in that effects of spin-orbit and related interactions are neglected entirely and the crystal field is assumed sufficiently weak so that it does not mix together different free-ion levels. (These two assumptions together constitute the so-called "weak-field approximation."\(^{3-5}\)) Also, we use the simplest model to describe the host lattice, the point-charge model. Refinements of this model, such as dipole\(^6\) and self-induced\(^7\) contributions to the crystal field, considered elsewhere for rare-earth ions, are not included in this work.

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*The theory for rare-earth ions is discussed in a sequence of 14 technical reports of Harry Diamond Laboratories published between October 1973 and February 1977, entitled Rare Earth Ion-Host Interactions.
2. THEORY

In the weak-field approximation, it is assumed that the mutual Coulomb interactions among the \( d^N \) electrons in the free ion are much larger than the same interaction of these electrons with the crystalline field. Also, both the Coulomb interaction and the interaction with the crystal field are assumed much larger than the spin-orbit interaction. Thus, in the remainder of the discussion, we shall ignore the spin-orbit interaction. For the \( 3d^N \) series, these assumptions are quite good, but they become less valid\(^5\) for \( n = 4 \) or 5.

The Coulomb interaction within the \( nd^N \) configuration can be written as\(^8\)

\[
H_c = \frac{1}{2} \sum_{i \neq j}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|},
\]
or

\[
H_c = \sum_{k}^N \sum_{i \neq j} F(k) C_{kq}(\mathbf{r}_i) C_{kq}(\mathbf{r}_j),
\]

where the \( F(k) \) (Slater parameters) are given by

\[
F(k) = 2e^2 \int_0^\infty R^2_{nd}(r) \, dr \int_0^\infty R^2_{nd}(r') \, \frac{r}{r+k+1} \, dr'. \tag{2}
\]

For \( d \) electrons only terms in equation (1) with \( k \leq 4 \) have nonvanishing matrix elements, and thus only \( F(2) \) and \( F(4) \) are needed. The \( C_{kq}(r) \) are unnormalized spherical tensors related to the more familiar spherical harmonics \( Y_{kq}(r) \) by

\[
C_{kq}(\mathbf{r}) = \sqrt{\frac{4\pi}{2k+1}} Y_{kq}(\mathbf{r}).
\]

The matrix elements of the Coulomb interaction are given by Nielson and Koster\(^9\) in the form

\[
\langle \alpha' \mathbf{L'S'} | H_c | \alpha LS \rangle = \delta_{LL'} \delta_{SS'} \sum_k c_k(\alpha', \alpha, L, S) F(k), \tag{3}
\]

the coefficients \( c_k(\alpha', \alpha, L, S) \) are tabulated elsewhere\(^9\) for each of the states of \( d^N \) for \( 1 \leq N \leq 3 \). For \( N > 3 \) the matrix elements of \( d^{10-N} \) are identical to those of \( d^N \).


Eigenstates of the Coulomb interaction are found by diagonalizing the matrix formed by equation (3) for a given \( L \) and \( S \). For states of maximum multiplicity, there is only one state for a given \( L \) and \( S \); in particular, the Hund ground states have \( S \) as the maximum possible value (\( = N/2 \) for \( N \leq 5 \)) and \( L \) the maximum value consistent with \( S \) (\( = N(7 - N)/2 \) for \( N \leq 5 \)). Thus the Hund ground states are \( 2D, 3F, 4F, 5D, \) and \( 6S \) for \( d^1, d^2, d^3, d^4, \) and \( d^5 \), respectively. For \( N > 5 \), Hund ground states of \( d^N \) are the same as those for \( d^{10-N} \). The Slater parameters are obtained either by being fit to experimental data or by being calculated using Hartree-Fock wave functions.\(^{10}\) In general, the Hartree-Fock \( F(k) \) are much larger than the corresponding \( F \) obtained by fitting to the experimental data on free ions. Further, the \( F(k) \) for ions in crystals are reduced compared with their free-ion values.*

The interaction of the \( d^N \) electrons with the crystal field is taken as

\[
H_{CEF} = \sum_{nm} B^* \sum_i C_{nm}^{\dagger} r_i \tag{4}
\]

where, for \( d \) electrons, \( n = 2 \) and \( 4 \) only, and where the allowed values of \( m \) depend on the crystal symmetry. The crystal-field interaction given in equation (4) can be written in terms of Racah's unit tensors\(^{11}\) as

\[
H_{CEF} = \frac{\sqrt{10}}{7} \sum_n (-1)^{n/2} B^* U^{(n)} \tag{5}
\]

The matrix elements of the unit tensors, \( U_m(n) \), in equation (5) can be calculated using the Wigner-Eckart theorem to give

\[
\langle \alpha 'L'N'S'M'_S | U_m^{(n)} | L'M_S S \rangle = \frac{\langle L(N_L) | n(m) | L'(M'_L) \rangle}{\sqrt{2L' + 1}} \frac{(\alpha 'L'S) | (n) | (\alpha LS) \delta_{SS} \delta_{M'M'_S}}{\delta_{L'L} \delta_{M_M_S}} \tag{6}
\]

where the reduced matrix elements, \( (\alpha 'L'S) | (n) | (\alpha LS) \), are tabulated (with no additional factors) elsewhere.\(^9\) The quantity in angular brackets in equation (6) is a Clebsch-Gordan coefficient (proportional to a 3-j symbol) and is

\[\text{C. W. Nielson and G. F. Koster, Spectroscopic Coefficients for the } p^N, d^N \text{ and } f^N \text{ Configurations, The MIT Press, Cambridge, MA (1963), p 53.}\]

\[\text{B. G. Wybourne, Spectroscopic Properties of Rare Earths, Interscience Publishers, New York (1965).}\]


*The theory for rare-earth ions is discussed in a sequence of 14 technical reports of Harry Diamond Laboratories published between October 1973 and February 1977, entitled Rare Earth Ion-Host Interactions.
Thus the calculation of the crystal-field splittings can be performed once the crystal-field parameters, \( B_{nm} \), are known.

In the point-charge model* of the crystal field, the parameters \( B_{nm} \) are given by

\[
B_{nm} = \langle r^n \rangle A_{nm} 
\]  

(7)

where \( \langle r^n \rangle \) is the radial expectation value of \( r^n \) calculated using Hartree-Fock wave functions, and the \( A_{nm} \) are the coefficients of a multipolar expansion of the crystal field at the site occupied by the transition-metal ion. The \( A_{nm} \) have been evaluated for the \( S_4 \) and \( D_{2d} \) sites (equivalent for the \( d \) configuration) in a number of solids.\(^{13} \)

Frequently in the analysis of the spectra of a transition-metal ion in a solid, a cubic-field approximation is made; however, there seems to be no consistent method of making this approximation. For example, suppose the ion were in \( S_4 \) symmetry; then the nonvanishing crystal-field parameters are \( B_{20} \), \( B_{40} \), and \( B_{44} \). In any cubic approximation, \( B_{20} \) is assumed to be zero. The question is how to select the best cubic \( B_{nm}^c \) from the \( B_{40} \) and \( B_{44} \) corresponding to \( S_4 \) symmetry. Recently,\(^{14} \) the role of the rotational invariants given by

\[
\Xi_n = \left[ \frac{1}{2n + 1} \sum_{nm} B_{nm}^* B_{nm} \right]^{1/2} 
\]  

(8)

has been discussed. The \( \Xi_n \) have the property of invariance under arbitrary coordinate rotation. The choice of \( B_{40}^c \) can be made unique by requiring that the corresponding \( \Xi_4 \) parameters in \( S_4 \) and cubic symmetries be equal. We have

\[
B_{40}^c = \lambda B_{40} 
\]  

(9)

where

\[
\lambda = \left[ 7(1 + 2B_{44}^2/B_{40}^2) / 12 \right]^{1/2} 
\]  

(10)

where we have used the relation \( B_{44}^c = 5B_{40}^c / 70 \) as required in the cubic groups.

\(^{12} \)M. Rotenberg, R. Bivins, N. Metropolis, and J. Wooten, Jr., The 3-j and 6-j Symbols, Technology Press, Massachusetts Institute of Technology, Cambridge, MA (1959).

\(^{13} \)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).


*The theory for rare-earth ions is discussed in a sequence of 14 technical reports of Harry Diamond Laboratories published between October 1973 and February 1977, entitled Rare Earth Ion-Host Interactions.
3. LATTICE SUMS FOR Gd$_3$Sc$_2$Ga$_3$O$_{12}$

The crystallographic and x-ray data$^{15}$ on GSGG are given in Table 1. Also contained in the table are the ionic radii$^{16}$ and the effective charges of the constituent ions. Six oxygen ions surround the Sc$^{3+}$ ion at a distance of 2.04 Å, and four oxygen ions surround the Ga$^{3+}$ ion at a distance of 1.89 Å. (From the ionic radii we obtain 2.13 Å and 1.87 Å, respectively.) When the crystal is doped with an ion, it is important that the ionic radius of the dopant ion nearly match the ionic radius of the constituent ion it is to replace. The point-charge contributions to the $A$ were calculated$^t$ using the data given in Table 1; the results are $A_{20} = 739 \text{ cm}^{-1}/\text{Å}^2$, $A_{40} = -13,749 \text{ cm}^{-1}/\text{Å}^4$, and $A_{44} = 5,515 \text{ cm}^{-1}/\text{Å}^4$. (The coordinate system has been rotated so that $A_{44}$ is real and positive.)

### Table 1. Crystallographic and X-ray Data, Ionic Radii, and Effective Charges for Gd$_3$Sc$_2$Ga$_3$O$_{12}$

<table>
<thead>
<tr>
<th>Ion</th>
<th>Site</th>
<th>Cubic Space Group Ia3d, No. 230, Z = 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd</td>
<td>24(c)</td>
<td>D$_2$, 0, 1/4, 1/8, 1.06, 3</td>
</tr>
<tr>
<td>Sc</td>
<td>16(a)</td>
<td>C$_{3h}$, 0, 0, 0, 0.73, 3</td>
</tr>
<tr>
<td>Ga</td>
<td>24(d)</td>
<td>S$_2$, 3/8, 0, 1/4, 0.47, 3</td>
</tr>
<tr>
<td>O$^6$</td>
<td>96(h)</td>
<td>C$_1$, -0.0202, 0.0558, 0.1501, 1.40, -2</td>
</tr>
</tbody>
</table>


$^*10 \text{ Å} = 1 \text{ nm}$.


4. THE d$^1$ AND d$^9$ CONFIGURATIONS

Table 2 gives the values, where known, of $<r^2>$, $<r^4>$, ionic radii (i.r.), and energy of the next configuration above the ground configuration relative to the ground state (Δ) for a number of ions with the configurations nd$^1$ and nd$^9$. 


The ions given in table 2 were chosen because data exist on them concerning crystal growth, optical spectra, or electron spin resonance. Unfortunately, Fraga et al. do not calculate values of \( <r^k> \) for ionization states greater than 3 for the \( \text{nd}^N \) ions. Thus, we cannot complete the crystal-field calculations on these highly ionized ions.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Configuration</th>
<th>( &lt;r^2&gt; (\text{Å}^2) )</th>
<th>( &lt;r^4&gt; (\text{Å}^4) )</th>
<th>i.r.</th>
<th>( \Delta ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ti}^{3+} )</td>
<td>3d(^1)</td>
<td>0.5341</td>
<td>0.5769</td>
<td>0.67</td>
<td>80,389(^2)</td>
</tr>
<tr>
<td>( \text{V}^{4+} )</td>
<td>3d(^1)</td>
<td>---</td>
<td>---</td>
<td>0.59</td>
<td>148,143(^2)</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} )</td>
<td>3d(^9)</td>
<td>0.2489</td>
<td>0.2097</td>
<td>0.62</td>
<td>12,600(^2)</td>
</tr>
<tr>
<td>( \text{Zn}^{3+} )</td>
<td>3d(^9)</td>
<td>0.2297</td>
<td>0.1200</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>( \text{W}^{9+} )</td>
<td>4d(^1)</td>
<td>---</td>
<td>---</td>
<td>0.69</td>
<td>74,000(^2)</td>
</tr>
<tr>
<td>( \text{Mo}^{5+} )</td>
<td>4d(^9)</td>
<td>0.6899</td>
<td>0.9612</td>
<td>0.59</td>
<td>31,500(^2)</td>
</tr>
<tr>
<td>( \text{Ag}^{2+} )</td>
<td>4d(^9)</td>
<td>0.5516</td>
<td>0.5644</td>
<td>0.89</td>
<td>63,000(^2)</td>
</tr>
<tr>
<td>( \text{Ta}^{6+} )</td>
<td>5d(^1)</td>
<td>---</td>
<td>---</td>
<td>0.66</td>
<td>---</td>
</tr>
</tbody>
</table>

\(^a\)Values of \( <r^D> \) are from reference 17 and ionic radii are from reference 16. The quantity \( \Delta \) is the energy of the next configuration relative to the ground configuration relative to the ground state.

\(^b\)i.r. = ionic radius.


\(^e\)For 4 coordination.


\(^g\)For 2 coordination.

The matrix elements of the crystal field were computed using equation (7); the results are given in table 3. The notation for the irreducible representations (IR) of \( S_4 \) is that of Koster et al. Since in the \( S_4 \) group the energy levels for \( \Gamma_3 \) and \( \Gamma_4 \) are degenerate, the matrix elements for \( \Gamma_3 \) are omitted. Using the results from table 2, we calculated the crystal-field parameters, \( B_{nm} \), for the \( \text{Ga}^{3+} \) site in GSGG. These results are given in table 4 along with the cubic \( B_0^c \) obtained from equation (10). The energy levels of \( d^1 \) and \( d^9 \) ions were computed using the data in tables 3 and 4, and the results are given in table 5. Note that levels of \( d^9 \) are inverted relative to levels of \( d^1 \). The results for \( \text{Ti}^{3+} \) indicate that unless the crystal field is severely underestimated and the next electronic configuration is lowered

\(^3\)C. W. Nielson and G. F. Koster, Spectroscopic Coefficients for the p\(^n\), d\(^n\) and f\(^n\) Configurations, The MIT Press, Cambridge, MA (1963), p 53.

\(^{17}\)S. Fraga, J. Karwowski, and K. M. S. Saxena, Physical Sciences Data, Vol. 5, Handbook of Atomic Data, Elsevier/North-Holland, New York (1976). [The values of \( <r^k> \) are not reported for ionization states greater than 3.]

considerably, only the far-infrared spectrum of this ion would be observed. The relatively small splittings of the Zn\(^{3+}\) ion and the relatively large value for \(\zeta\), the spin-orbit parameter,\(^{17}\) indicate that more accurate levels for this ion would be obtained by diagonalizing simultaneously the crystal-field and spin-orbit interactions within the 2D state.

**TABLE 3. MATRIX ELEMENTS IN S\(_4\) SYMMETRY OF CRYSTAL FIELD FOR 2D STATE OF nd\(^1\) AND 5D STATE OF nd\(^6\)**

Note: For the corresponding matrix elements for the 2D state of nd\(^3\) and the 5D state of nd\(^4\), multiply all entries by \(-1\).\(^a\)

<table>
<thead>
<tr>
<th>M'</th>
<th>M</th>
<th>IR(^b)</th>
<th>B(_{20})</th>
<th>B(_{40})</th>
<th>B(_{44})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>(\Gamma_1)</td>
<td>2/7</td>
<td>2/7</td>
<td>0</td>
</tr>
<tr>
<td>-2</td>
<td>-2</td>
<td>(\Gamma_2)</td>
<td>-2/7</td>
<td>1/21</td>
<td>0</td>
</tr>
<tr>
<td>-2</td>
<td>2</td>
<td>(\Gamma_2)</td>
<td>0</td>
<td>0</td>
<td>(\sqrt{70}/21)</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>(\Gamma_2)</td>
<td>-2/7</td>
<td>1/21</td>
<td>0</td>
</tr>
<tr>
<td>-1</td>
<td>-1</td>
<td>(\Gamma_4)</td>
<td>1/7</td>
<td>-4/21</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\)The matrix elements of \(\Gamma_3\) are not given, as they are equal to those for \(\Gamma_4\).  
\(^b\)IR = irreducible representation.

**TABLE 4. CRYSTAL-FIELD PARAMETERS, B\(_{nm}\) (cm\(^{-1}\)), FOR nd\(^1\) AND nd\(^9\) IONS IN Ga\(^{3+}\) SITE IN GSGG**

<table>
<thead>
<tr>
<th>Ion</th>
<th>B(_{20})</th>
<th>B(_{40})</th>
<th>B(_{44})</th>
<th>B(_{40})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(^{3+})</td>
<td>394.7</td>
<td>-7,932</td>
<td>3,182</td>
<td>-6,965</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>184.0</td>
<td>-2,883</td>
<td>1,156</td>
<td>-2,531</td>
</tr>
<tr>
<td>Zn(^{3+})</td>
<td>169.8</td>
<td>-1,649</td>
<td>661.6</td>
<td>-1,448</td>
</tr>
<tr>
<td>Pd(^{1+})</td>
<td>509.9</td>
<td>-13,215</td>
<td>5,301</td>
<td>-11,604</td>
</tr>
<tr>
<td>Ag(^{2+})</td>
<td>407.6</td>
<td>-7,759</td>
<td>3,112</td>
<td>-6,813</td>
</tr>
</tbody>
</table>

**TABLE 5. ENERGY LEVELS (cm\(^{-1}\)) FOR 2D LEVEL OF nd\(^1\) AND nd\(^9\) IONS IN Ga\(^{3+}\) SITE OF GSGG**

<table>
<thead>
<tr>
<th>IR(^a)</th>
<th>(\Gamma_1)</th>
<th>(\Gamma_2)</th>
<th>(\Gamma_2)</th>
<th>(\Gamma_{3,4})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(^{3+})</td>
<td>0</td>
<td>395</td>
<td>2,930</td>
<td>3,720</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>1,346</td>
<td>1,225</td>
<td>304</td>
<td>0</td>
</tr>
<tr>
<td>Zn(^{3+})</td>
<td>761</td>
<td>729</td>
<td>201</td>
<td>0</td>
</tr>
<tr>
<td>Pd(^{1+})</td>
<td>6,220</td>
<td>5,476</td>
<td>1,253</td>
<td>0</td>
</tr>
<tr>
<td>Ag(^{2+})</td>
<td>3,636</td>
<td>3,262</td>
<td>732</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\)IR = irreducible representation.

\(^{17}\)S. Fraga, J. Karwowski, and K. M. S. Saxena, Physical Sciences Data, Vol. 5, Handbook of Atomic Data, Elsevier/North-Holland, New York (1976). [The values of \(<r^k>\) are not reported for ionization states greater than 3.]
5. THE \( d^2 \) AND \( d^8 \) CONFIGURATIONS

The Hund ground state for nd\(^2\) is \( 3F \). The ions with \( d^2 \) and \( d^8 \) configurations selected for investigation in the Ga\(^{3+}\) site in GSGG are given in Table 6. The ionic radii of the ions given in Table 6 are for coordination number 6 and are considerably larger than the i.r. for Ga\(^{3+}\) in 4 coordination. However, if say V\(^{3+}\) could be substituted into the 4 coordination site, the i.r. would be considerably reduced (the i.r. for Ga\(^{3+}\) is 0.47 Å for 4 coordination and 0.620 Å for 6 coordination\(^{16}\)). Of the ions with the \( d^8 \) configuration, it would appear that Ni\(^{2+}\) has the best chance of replacing Ga\(^{3+}\) in GSGG. The matrix elements of the crystal-field interaction for the \( 3F \) state of nd\(^2\) are given in Table 7. The largest matrix is 2 x 2, which occurs for the \( \Gamma_2 \) and the \( \Gamma_3,4 \) doublets. The crystal-field parameters for the Ga\(^{3+}\) site in GSGG given in Table 8 were computed using the results of Tables 6 and 7. The crystal-field parameters were used to compute the energy levels of the 10 ions given in Table 6; the results are given in Table 9 (p. 14). For the V\(^{3+}\) ion, the total crystal-field splitting is small (4,600 cm\(^{-1}\)) compared to the free-ion splitting (16,700 cm\(^{-1}\)), so that the influence of the next configuration, \( 3P \), can be ignored in a first approximation. However, for Ti\(^{2+}\), the free-ion energy separation \( 3F-3P \) and the crystal-field splittings are the same order of magnitude, so that a more precise crystal-field calculation must include the \( 3P \) state. In the case of Nb\(^{3+}\), the crystal-field splitting is much larger than the free-ion energy spacing of the \( 3F-3P \) levels, which

### Table 6. Data on Ions with nd\(^2\) and nd\(^8\) Configurations

<table>
<thead>
<tr>
<th>Ion</th>
<th>Configuration</th>
<th>(&lt;r^2&gt;(\text{Å}^2))</th>
<th>(&lt;r^4&gt;(\text{Å}^4))</th>
<th>i.r.(^{b}) (Å)</th>
<th>(\Delta) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(^{2+})</td>
<td>3d(^2)</td>
<td>0.6716</td>
<td>0.9808</td>
<td>0.86</td>
<td>10,419(^c)</td>
</tr>
<tr>
<td>V(^{3+})</td>
<td>3d(^2)</td>
<td>0.4571</td>
<td>0.4270</td>
<td>0.64</td>
<td>16,700(^d)</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>3d(^8)</td>
<td>0.3203</td>
<td>0.2478</td>
<td>0.69</td>
<td>8,500(^e)</td>
</tr>
<tr>
<td>Nb(^{3+})</td>
<td>4d(^2)</td>
<td>0.9282</td>
<td>1.4606</td>
<td>0.70</td>
<td>9,000(^f)</td>
</tr>
<tr>
<td>Rh(^{4+})</td>
<td>4d(^2)</td>
<td>0.7682</td>
<td>1.1872</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Pd(^{2+})</td>
<td>4d(^8)</td>
<td>0.6045</td>
<td>0.6744</td>
<td>0.64(^f)</td>
<td>10,600(^e)</td>
</tr>
<tr>
<td>Ag(^{3+})</td>
<td>4d(^8)</td>
<td>0.4993</td>
<td>0.4372</td>
<td>0.65(^f)</td>
<td>---</td>
</tr>
<tr>
<td>Ta(^{3+})</td>
<td>5d(^2)</td>
<td>1.0416</td>
<td>1.7777</td>
<td>0.67</td>
<td>---</td>
</tr>
<tr>
<td>Pt(^{2+})</td>
<td>5d(^8)</td>
<td>0.7474</td>
<td>0.9649</td>
<td>0.60(^f)</td>
<td>---</td>
</tr>
<tr>
<td>Au(^{3+})</td>
<td>5d(^8)</td>
<td>0.6357</td>
<td>0.6646</td>
<td>0.70(^f)</td>
<td>---</td>
</tr>
</tbody>
</table>

\(^a\)Values of \(<r^2>\) and ionic radius are from references 17 and 16, respectively. The quantity \(\Delta\) is the difference in energy between \(3P\) and \(3F\) states in the free ion.

\(^b\)I.r. = ionic radius.


\(^f\)For 4 coordination.


---

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indicates that even for a first estimate of the splittings, both the $^{3}\text{P}$ and $^{3}\text{F}$ levels should be included. Because of the large values of $\zeta$ for the $d^8$ ions, the approximations used in the calculations for these ions are probably poor, the only exception being perhaps Ni$^{2+}$.

**TABLE 7. MATRIX ELEMENTS IN $S_4$ SYMMETRY OF CRYSTAL FIELD FOR $^3\text{P}$ STATE OF nd$^2$**

<table>
<thead>
<tr>
<th>N</th>
<th>M</th>
<th>$\text{IR}^b$</th>
<th>$B_{20}$</th>
<th>$B_{40}$</th>
<th>$B_{44}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>$\Gamma_1$</td>
<td>4/35</td>
<td>-2/7</td>
<td>0</td>
</tr>
<tr>
<td>-2</td>
<td>-2</td>
<td>$\Gamma_2$</td>
<td>0</td>
<td>1/3</td>
<td>0</td>
</tr>
<tr>
<td>-2</td>
<td>2</td>
<td>$\Gamma_2$</td>
<td>0</td>
<td>0</td>
<td>-70/21</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>$\Gamma_2$</td>
<td>0</td>
<td>1/3</td>
<td>0</td>
</tr>
<tr>
<td>-1</td>
<td>-1</td>
<td>$\Gamma_4$</td>
<td>3/35</td>
<td>-1/21</td>
<td>0</td>
</tr>
<tr>
<td>-1</td>
<td>3</td>
<td>$\Gamma_4$</td>
<td>0</td>
<td>0</td>
<td>-82/21</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>$\Gamma_4$</td>
<td>-1/7</td>
<td>-1/7</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$The matrix elements of $\Gamma_3$ are not given, as they are equal to those for $\Gamma_4$.

$^b$IR = irreducible representation.

**TABLE 8. CRYSTAL-FIELD PARAMETERS, $B_{nm}$ (cm$^{-1}$), FOR nd$^2$ and nd$^8$ IONS IN Ga$^{3+}$ SITE IN GSGG**

<table>
<thead>
<tr>
<th>Ion</th>
<th>$B_{20}$</th>
<th>$B_{40}$</th>
<th>$B_{44}$</th>
<th>$B_{40}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$^{2+}$</td>
<td>496.3</td>
<td>-13,485</td>
<td>5,409</td>
<td>-11,800</td>
</tr>
<tr>
<td>V$^{3+}$</td>
<td>337.8</td>
<td>-5,870</td>
<td>2,355</td>
<td>-5,155</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>236.7</td>
<td>-3,407</td>
<td>1,367</td>
<td>-2,992</td>
</tr>
<tr>
<td>Nb$^{3+}$</td>
<td>685.9</td>
<td>-20,082</td>
<td>8,055</td>
<td>-17,634</td>
</tr>
<tr>
<td>Rh$^{3+}$</td>
<td>567.7</td>
<td>-16,323</td>
<td>6,548</td>
<td>-14,334</td>
</tr>
<tr>
<td>Pd$^{2+}$</td>
<td>446.7</td>
<td>-9,272</td>
<td>3,719</td>
<td>-8,142</td>
</tr>
<tr>
<td>Ag$^{3+}$</td>
<td>369.0</td>
<td>-6,011</td>
<td>2,411</td>
<td>-5,278</td>
</tr>
<tr>
<td>Ta$^{3+}$</td>
<td>769.8</td>
<td>-24,442</td>
<td>9,804</td>
<td>-21,652</td>
</tr>
<tr>
<td>Pt$^{2+}$</td>
<td>552.3</td>
<td>-13,267</td>
<td>5,322</td>
<td>-11,650</td>
</tr>
<tr>
<td>Au$^{3+}$</td>
<td>469.7</td>
<td>-9,138</td>
<td>3,665</td>
<td>-8,024</td>
</tr>
</tbody>
</table>

6. THE $d^3$ AND $d^7$ CONFIGURATIONS

A number of ions with nd$^3$ or nd$^7$ configurations are listed in table 10 along with the $<\kappa^2>$, i.r., and $\Delta$ values. Most of these ions could have small enough i.r. in 4 coordination to fit in the Ga$^{3+}$ site if methods could be found to properly dope the crystal. Because of the relative importance of Cr$^{3+}$ in GSGG, we have included the matrix elements of the crystal field in both $^4\text{F}$ and $^4\text{P}$ states in table 11. The calculations reported here only involve the $^4\text{F}$ part of the crystal-field matrix, but further work will employ all the matrix elements given in table 11.

$^{17}$S. Fraga, J. Karwowski, and K. M. S. Saxena, Physical Sciences Data, Vol. 5, Handbook of Atomic Data, Elsevier/North-Holland, New York (1976). [The values of $<\kappa^2>$ are not reported for ionization states greater than 3.]
TABLE 9. ENERGY LEVELS (cm\(^{-1}\)) FOR \(^3\)F LEVEL OF nd\(^2\) AND nd\(^8\) IONS IN Ga\(^3+\) SITE OF GSGG

<table>
<thead>
<tr>
<th>Ion</th>
<th>(r_1)</th>
<th>(r_2)</th>
<th>(r_3,4)</th>
<th>(r_3,4)</th>
<th>(r_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(^{2+})</td>
<td>0</td>
<td>4.310</td>
<td>6.151</td>
<td>9.688</td>
<td>10.559</td>
</tr>
<tr>
<td>V(^{3+})</td>
<td>0</td>
<td>1.876</td>
<td>2.678</td>
<td>4.209</td>
<td>4.610</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>2.680</td>
<td>1.591</td>
<td>1.125</td>
<td>239</td>
<td>0</td>
</tr>
<tr>
<td>Nb(^{3+})</td>
<td>0</td>
<td>6.418</td>
<td>9.159</td>
<td>14.432</td>
<td>15.719</td>
</tr>
<tr>
<td>Rh(^{4+})</td>
<td>12.778</td>
<td>7.561</td>
<td>5.332</td>
<td>1.047</td>
<td>0</td>
</tr>
<tr>
<td>Pd(^{2+})</td>
<td>7.272</td>
<td>4.308</td>
<td>3.042</td>
<td>617</td>
<td>0</td>
</tr>
<tr>
<td>Ag(^{3+})</td>
<td>4.723</td>
<td>2.802</td>
<td>1.980</td>
<td>414</td>
<td>0</td>
</tr>
<tr>
<td>Ta(^{5+})</td>
<td>0</td>
<td>7.012</td>
<td>11.147</td>
<td>17.570</td>
<td>19.124</td>
</tr>
<tr>
<td>Pd(^{2+})</td>
<td>10.396</td>
<td>6.155</td>
<td>4.343</td>
<td>867</td>
<td>0</td>
</tr>
<tr>
<td>Au(^{3+})</td>
<td>7.170</td>
<td>4.250</td>
<td>3.001</td>
<td>613</td>
<td>0</td>
</tr>
</tbody>
</table>

\(a\)IR = irreducible representation.

TABLE 10. DATA ON IONS WITH \(nd^3\) AND \(nd^7\) CONFIGURATIONS

<table>
<thead>
<tr>
<th>Ion</th>
<th>Configuration</th>
<th>(&lt;r^2&gt;(A^2))</th>
<th>(&lt;r^4&gt;(A^4))</th>
<th>i.r. ((\text{\AA}))</th>
<th>(\Delta (\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(^{2+})</td>
<td>(3d^3)</td>
<td>0.5677</td>
<td>0.7112</td>
<td>0.79</td>
<td>12,600(^c)</td>
</tr>
<tr>
<td>Cr(^{3+})</td>
<td>(3d^3)</td>
<td>0.4018</td>
<td>0.3344</td>
<td>0.615</td>
<td>17,400(^d)</td>
</tr>
<tr>
<td>Co(^{2+})</td>
<td>(3d^7)</td>
<td>0.3525</td>
<td>0.2949</td>
<td>0.65</td>
<td>(-14,000)^e</td>
</tr>
<tr>
<td>Ni(^{3+})</td>
<td>(3d^7)</td>
<td>0.2705</td>
<td>0.1615</td>
<td>0.56</td>
<td>(-16,000)^e</td>
</tr>
<tr>
<td>Nb(^{2+})</td>
<td>(4d^3)</td>
<td>1.0769</td>
<td>2.0761</td>
<td>0.71</td>
<td>24,800(^c),(^g)</td>
</tr>
<tr>
<td>Mo(^{3+})</td>
<td>(4d^5)</td>
<td>0.9288</td>
<td>1.1461</td>
<td>0.67</td>
<td>60,000(^c),(^g)</td>
</tr>
<tr>
<td>Pd(^{3+})</td>
<td>(4d^7)</td>
<td>0.5435</td>
<td>0.5147</td>
<td>0.76</td>
<td>---</td>
</tr>
<tr>
<td>W(^{4+})</td>
<td>(5d^3)</td>
<td>0.9400</td>
<td>1.4438</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

\(a\)Values of \(<r^n>\) and ionic radius are from references 17 and 16, respectively. The quantity \(\Delta\) is the difference in energy between \(^4\)F and \(^4\)P states in the free ion.

\(b\)i.r. = ionic radius.


\(h\)\(\Delta\) is the difference in energy between \((4d^55s)^4F\) and \((4d^3)^4F\) in the free ion.

Table 12 gives the crystal-field parameters computed from the results given in tables 10 and 11. Of the ions with the \(nd^3\) configuration, the largest crystal-field parameters are for Nb\(^{2+}\); from the results given in table 13 (p 16) it would appear that all the matrix elements given in table 11 should be used in the calculation. However, it does not appear that using the full matrix will appreciably affect the levels of Cr\(^{3+}\), since the crystal-field splitting is only 3,614 cm\(^{-1}\) and the \(^4\)F-\(^4\)P levels are split by 17,400 cm\(^{-1}\). For both Ni\(^{3+}\) and Co\(^{2+}\), the approximations used in the calculations are reasonable. However, the value of \(\zeta\) for Pd\(^{3+}\) and the proximity of several excited states indicate that a reasonable calculation for this ion would include several states of 4d\(^7\).
TABLE 11. MATRIX ELEMENTS, IN \( S_4 \) SYMMETRY, OF CRYSTAL FIELD FOR \( 4F \) AND \( 4P \) STATES OF \( nd^3 \)

Note: For the corresponding matrix elements for \( 4F \) and \( 4P \) states of \( nd^7 \), multiply all entries by \(-1\).

<table>
<thead>
<tr>
<th>( L'M' )</th>
<th>( L M )</th>
<th>( IR^b )</th>
<th>( B_{20} )</th>
<th>( B_{40} )</th>
<th>( B_{44} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 0</td>
<td>3 0</td>
<td>( \Gamma_1 )</td>
<td>-4/35</td>
<td>2/7</td>
<td>0</td>
</tr>
<tr>
<td>3 0</td>
<td>1 0</td>
<td>( \Gamma_1 )</td>
<td>12/35</td>
<td>-4/21</td>
<td>0</td>
</tr>
<tr>
<td>1 0</td>
<td>1 0</td>
<td>( \Gamma_1 )</td>
<td>2/5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3-2</td>
<td>3-2</td>
<td>( \Gamma_2 )</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3-2</td>
<td>3 2</td>
<td>( \Gamma_2 )</td>
<td>0</td>
<td>0</td>
<td>1/7/21</td>
</tr>
<tr>
<td>3 2</td>
<td>3 2</td>
<td>( \Gamma_2 )</td>
<td>0</td>
<td>-1/3</td>
<td>0</td>
</tr>
<tr>
<td>3-1</td>
<td>3-1</td>
<td>( \Gamma_4 )</td>
<td>-3/35</td>
<td>1/21</td>
<td>0</td>
</tr>
<tr>
<td>3-1</td>
<td>3 3</td>
<td>( \Gamma_4 )</td>
<td>0</td>
<td>0</td>
<td>1/21</td>
</tr>
<tr>
<td>3-1</td>
<td>1-1</td>
<td>( \Gamma_4 )</td>
<td>2/8/35</td>
<td>4/21</td>
<td>0</td>
</tr>
<tr>
<td>3 3</td>
<td>3 3</td>
<td>( \Gamma_4 )</td>
<td>1/7</td>
<td>1/7</td>
<td>0</td>
</tr>
<tr>
<td>3 3</td>
<td>1-1</td>
<td>( \Gamma_4 )</td>
<td>0</td>
<td>0</td>
<td>2/7/21</td>
</tr>
<tr>
<td>3-1</td>
<td>1-1</td>
<td>( \Gamma_4 )</td>
<td>-1/5</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\( ^a \)The matrix elements of \( \Gamma_3 \) are not given, as they are equal to those for \( \Gamma_4 \). Before the matrix is diagonalized, the Coulomb energies from equation (3) for the \( 4F \) and \( 4P \) states should be added to the diagonal elements.

\( ^b \)IR = irreducible representation.

TABLE 12. CRYSTAL-FIELD PARAMETERS, B \( \text{(cm}^{-1}) \), FOR \( nd^3 \) AND \( nd^7 \) IONS IN Ga\(^{3+}\) SITE IN GSGG

<table>
<thead>
<tr>
<th>Ion</th>
<th>( B_{20} )</th>
<th>( B_{40} )</th>
<th>( B_{44} )</th>
<th>( B_{40} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(^2+)</td>
<td>419.5</td>
<td>-9,778</td>
<td>3,922</td>
<td>-8,586</td>
</tr>
<tr>
<td>Cr(^3+)</td>
<td>296.9</td>
<td>-4,597</td>
<td>1,844</td>
<td>-4,037</td>
</tr>
<tr>
<td>Mn(^3+)</td>
<td>260.5</td>
<td>-4,054</td>
<td>1,626</td>
<td>-3,560</td>
</tr>
<tr>
<td>Ni(^3+)</td>
<td>199.9</td>
<td>-2,221</td>
<td>890.8</td>
<td>-1,950</td>
</tr>
<tr>
<td>Fe(^3+)</td>
<td>795.8</td>
<td>-28,545</td>
<td>11,450</td>
<td>-25,065</td>
</tr>
<tr>
<td>Co(^3+)</td>
<td>686.4</td>
<td>-15,757</td>
<td>6,320</td>
<td>-13,836</td>
</tr>
<tr>
<td>Pd(^3+)</td>
<td>401.6</td>
<td>-7,077</td>
<td>2,839</td>
<td>-6,214</td>
</tr>
<tr>
<td>Os(^4+)</td>
<td>694.6</td>
<td>-19,851</td>
<td>7,963</td>
<td>-17,431</td>
</tr>
</tbody>
</table>

7. THE \( d^4 \) AND \( d^6 \) CONFIGURATIONS

Of the ions with \( nd^4 \) and \( nd^6 \) configurations listed in table 14, it would seem likely that \( Mn^{3+} \), \( Rh^{3+} \), or \( Ir^{3+} \) could be substituted for \( Ga^{3+} \) in GSGG. Unfortunately, the ions Os\(^4+\) and Ru\(^4+\) with quite small i.r. (which might possibly enter the \( 3^{3+} \) site) do not have reported values for \( \langle r^2 \rangle \). The matrix elements for the \( 5D \) state of the \( nd^4 \) and \( nd^5 \) configurations are given in table 3. The crystal-field parameters given in table 15 were used to
TABLE 13. ENERGY LEVELS (cm⁻¹) FOR ⁴F LEVEL OF nd³ AND nd⁷ IONS IN Ga³⁺ SITE OF GSGG

<table>
<thead>
<tr>
<th>Ion</th>
<th>Configuration</th>
<th>r₁</th>
<th>r₂,₄</th>
<th>r₃,₄</th>
<th>r₂</th>
<th>r₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>V²⁺</td>
<td>0</td>
<td>641</td>
<td>3,202</td>
<td>4,538</td>
<td>7,863</td>
<td></td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>0</td>
<td>319</td>
<td>1,516</td>
<td>2,145</td>
<td>3,614</td>
<td></td>
</tr>
<tr>
<td>Co²⁺</td>
<td>3,187</td>
<td>2,905</td>
<td>1,850</td>
<td>1,295</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Ni³⁺</td>
<td>1,752</td>
<td>1,588</td>
<td>1,013</td>
<td>709</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Nd²⁺</td>
<td>0</td>
<td>1,796</td>
<td>9,305</td>
<td>13,199</td>
<td>22,323</td>
<td></td>
</tr>
<tr>
<td>Mo³⁺</td>
<td>0</td>
<td>1,036</td>
<td>5,162</td>
<td>7,314</td>
<td>12,351</td>
<td></td>
</tr>
<tr>
<td>Pd³⁺</td>
<td>5,557</td>
<td>5,075</td>
<td>3,229</td>
<td>2,261</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>W³⁺</td>
<td>0</td>
<td>1,274</td>
<td>6,485</td>
<td>9,195</td>
<td>15,540</td>
<td></td>
</tr>
</tbody>
</table>

ₐIR = irreducible representation.

TABLE 14. DATA ON IONS WITH nd⁴ AND nd⁶ CONFIGURATIONS

<table>
<thead>
<tr>
<th>Ion</th>
<th>Configuration</th>
<th>&lt;r²&gt; (Å²)</th>
<th>&lt;r⁴&gt; (Å⁴)</th>
<th>i.r. (Å)</th>
<th>Δ (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr²⁺</td>
<td>3d⁶</td>
<td>0.4910</td>
<td>0.5401</td>
<td>0.73</td>
<td>13,900²</td>
</tr>
<tr>
<td>Mn³⁺</td>
<td>3d⁶</td>
<td>0.3578</td>
<td>0.2688</td>
<td>0.58</td>
<td>21,000²</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>3d⁶</td>
<td>0.3893</td>
<td>0.3527</td>
<td>0.63⁵</td>
<td>19,160⁶</td>
</tr>
<tr>
<td>Co³⁺</td>
<td>3d⁶</td>
<td>0.2947</td>
<td>0.1884</td>
<td>0.525</td>
<td>14,560⁸</td>
</tr>
<tr>
<td>Rh⁺</td>
<td>4d⁶</td>
<td>---</td>
<td>---</td>
<td>0.620</td>
<td>---</td>
</tr>
<tr>
<td>Ru⁺</td>
<td>4d⁶</td>
<td>0.5936</td>
<td>0.6094</td>
<td>0.665</td>
<td>---</td>
</tr>
<tr>
<td>Pd⁶⁺</td>
<td>4d⁶</td>
<td>---</td>
<td>---</td>
<td>0.62</td>
<td>---</td>
</tr>
<tr>
<td>Os⁴⁺</td>
<td>5d⁶</td>
<td>---</td>
<td>---</td>
<td>0.630</td>
<td>---</td>
</tr>
<tr>
<td>Ir³⁺</td>
<td>5d⁶</td>
<td>0.7309</td>
<td>0.8745</td>
<td>0.73</td>
<td>---</td>
</tr>
<tr>
<td>Pt⁴⁺</td>
<td>5d⁶</td>
<td>---</td>
<td>---</td>
<td>0.63</td>
<td>---</td>
</tr>
</tbody>
</table>

Values of <rⁿ> and ionic radius are from references 17 and 16, respectively. The quantity Δ is the difference in energy between ³H and ⁵D states in the free ion.

²i.r. = ionic radius.


₅For 4 coordination.


calculate the results given in table 16. For Mn³⁺, Fe²⁺, and Co³⁺, the crystal-field splittings are small compared to the spacing to the next free-ion level, so that ignoring the effects of these higher levels seems justified. However, the crystal-field splitting for Cr²⁺ is appreciable when compared to the 5D-3H separation given in table 14; thus, higher levels might have to be considered. Since the ground state has spin two and the next higher states have spin zero, the spin-orbit interaction must be considered in the calculation. The spin-orbit coupling constant, ζ, is quite small for both Mn³⁺ and Cr²⁺ but is quite large for Ru⁴⁺, Os⁴⁺, Ir³⁺, and Rh³⁺. In any serious investigation of these latter four ions, the spin-orbit interaction should be taken into consideration.

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TABLE 15. CRYSTAL-FIELD PARAMETERS, B\textsubscript{m} (cm\textsuperscript{-1}), FOR nd\textsuperscript{4} AND nd\textsuperscript{6} IONS IN Ga\textsuperscript{3+} SITE IN GSGG

<table>
<thead>
<tr>
<th>Ion</th>
<th>B\textsubscript{20}</th>
<th>B\textsubscript{40}</th>
<th>B\textsubscript{44}</th>
<th>B\textsubscript{40}^\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr\textsuperscript{2+}</td>
<td>362.8</td>
<td>-7,426</td>
<td>2,979</td>
<td>-6,521</td>
</tr>
<tr>
<td>Mn\textsuperscript{3+}</td>
<td>264.4</td>
<td>-3,695</td>
<td>1,482</td>
<td>-3,245</td>
</tr>
<tr>
<td>Fe\textsuperscript{2+}</td>
<td>287.7</td>
<td>-4,850</td>
<td>1,945</td>
<td>-4,258</td>
</tr>
<tr>
<td>Co\textsuperscript{3+}</td>
<td>217.8</td>
<td>-2,591</td>
<td>1,039</td>
<td>-2,275</td>
</tr>
<tr>
<td>Rh\textsuperscript{3+}</td>
<td>438.7</td>
<td>-8,379</td>
<td>3,361</td>
<td>-7,358</td>
</tr>
<tr>
<td>Ir\textsuperscript{3+}</td>
<td>540.1</td>
<td>-12,024</td>
<td>4,823</td>
<td>-10,558</td>
</tr>
</tbody>
</table>

TABLE 16. ENERGY LEVELS (cm\textsuperscript{-1}) FOR 5D LEVEL OF nd\textsuperscript{4} AND nd\textsuperscript{6} IONS IN Ga\textsuperscript{3+} SITE OF GSGG

<table>
<thead>
<tr>
<th>IR\textsuperscript{a}</th>
<th>\Gamma_{3,4}</th>
<th>\Gamma_{2}</th>
<th>\Gamma_{2}</th>
<th>\Gamma_{1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr\textsuperscript{2+}</td>
<td>0</td>
<td>736</td>
<td>3,110</td>
<td>3,484</td>
</tr>
<tr>
<td>Mn\textsuperscript{3+}</td>
<td>0</td>
<td>402</td>
<td>1,583</td>
<td>1,721</td>
</tr>
<tr>
<td>Fe\textsuperscript{2+}</td>
<td>2,268</td>
<td>1,765</td>
<td>215</td>
<td>0</td>
</tr>
<tr>
<td>Co\textsuperscript{3+}</td>
<td>1,202</td>
<td>906</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Rh\textsuperscript{3+}</td>
<td>3,927</td>
<td>3,083</td>
<td>405</td>
<td>0</td>
</tr>
<tr>
<td>Ir\textsuperscript{3+}</td>
<td>5,648</td>
<td>4,475</td>
<td>632</td>
<td>0</td>
</tr>
</tbody>
</table>

\textsuperscript{a}IR = irreducible representation.

8. THE d\textsuperscript{5} CONFIGURATION

The values of <k>, i.r., and \Delta for five ions with the nd\textsuperscript{5} configuration are given in table 17. Of these ions it seems quite likely that Fe\textsuperscript{3+} could be doped into the Ga\textsuperscript{3+} site in GSGG very easily. The crystal-field parameters for three of the ions listed in table 17 have been calculated using the results given there and in section 3. These crystal-field parameters are listed in table 18. Unfortunately, the ground state of the nd\textsuperscript{5} configuration is an S state and does not split in a crystal field unless the spin-orbit interaction is taken into consideration. The inclusion of the spin-orbit interaction mixes the states with spin 3/2, particularly the 4P state, into the ground state with spin 5/2. The 4P state would be coupled by the crystal field to a number of states with spin 3/2 (4G, etc.). These latter states are quite closely spaced in the free ion; consequently they all need to be taken into consideration in a realistic calculation. This procedure would lead to large matrices which would include the crystal-field, spin-orbit, and Coulomb interactions simultaneously. However, such a calculation could lead to some rather interesting results, particularly for Ir\textsuperscript{4+}, which has a very large \xi and should have a rather large splitting of the 6S ground state.
TABLE 17. DATA ON IONS WITH nd\textsuperscript{5} CONFIGURATION\textsuperscript{a}

<table>
<thead>
<tr>
<th>Ion</th>
<th>Configuration</th>
<th>&lt;\textit{r}^2&gt; (\textit{Å}\textsuperscript{2})</th>
<th>&lt;\textit{r}^4&gt; (\textit{Å}\textsuperscript{4})</th>
<th>i.r. \textsuperscript{b} (\textit{Å})</th>
<th>(\Delta) (cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn\textsuperscript{2+}</td>
<td>3d\textsuperscript{5}</td>
<td>0.4277</td>
<td>0.4145</td>
<td>0.839</td>
<td>26,846\textsuperscript{c}</td>
</tr>
<tr>
<td>Fe\textsuperscript{3+}</td>
<td>3d\textsuperscript{5}</td>
<td>0.3196</td>
<td>0.2168</td>
<td>0.49\textsuperscript{d}</td>
<td>-32,000\textsuperscript{e}</td>
</tr>
<tr>
<td>Ru\textsuperscript{3+}</td>
<td>4d\textsuperscript{5}</td>
<td>0.6479</td>
<td>0.7175</td>
<td>0.68</td>
<td>---</td>
</tr>
<tr>
<td>Rh\textsuperscript{3+}</td>
<td>4d\textsuperscript{5}</td>
<td>---</td>
<td>---</td>
<td>0.615</td>
<td>---</td>
</tr>
<tr>
<td>Ir\textsuperscript{3+}</td>
<td>5d\textsuperscript{5}</td>
<td>---</td>
<td>---</td>
<td>0.63</td>
<td>---</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Values of <\textit{r}^n> and ionic radius are from references 17 and 16, respectively. The quantity \(\Delta\) is the difference in energy between \(^4\text{G}\) and \(^6\text{S}\) states in the free ion.

\textsuperscript{b}i.r. \textsuperscript{b} = ionic radius.


\textsuperscript{d}For 4-coordination.


TABLE 18. CRYSTAL-FIELD PARAMETERS, \(B_n^{\text{HE}}\) (cm\textsuperscript{-1}), FOR nd\textsuperscript{5} IONS IN Ga\textsuperscript{3+} SITE IN GSGG

<table>
<thead>
<tr>
<th>Ion</th>
<th>(B_{20})</th>
<th>(B_{40})</th>
<th>(B_{44})</th>
<th>(B_{44}^{\text{HE}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn\textsuperscript{2+}</td>
<td>316.1</td>
<td>-5,699</td>
<td>2,286</td>
<td>-5,004</td>
</tr>
<tr>
<td>Fe\textsuperscript{3+}</td>
<td>236.2</td>
<td>-2,981</td>
<td>1,196</td>
<td>-2,618</td>
</tr>
<tr>
<td>Ru\textsuperscript{3+}</td>
<td>478.8</td>
<td>-9,865</td>
<td>3,957</td>
<td>-8,663</td>
</tr>
</tbody>
</table>

9. CONCLUSION AND SUGGESTIONS FOR FURTHER WORK

In our discussion of the crystal-field splittings of the Hund ground state of the nd\textsuperscript{N} configurations, particular ions were singled out for further work. Because of the lack of experimental data on ions in the particular host, Gd\textsubscript{3}Sc\textsubscript{2}Ga\textsubscript{2}O\textsubscript{12}, chosen for our investigation, either experimental work should be performed or we might shift our attention to different hosts where experimental data are available. If different hosts are considered, we would suggest attention towards fluorides rather than oxides, as it has been our experience in the study of rare-earth spectra\textsuperscript{*} that for the fluorides the point-charge model of crystal fields agrees well with experiment. In the oxides, the point-charge model has had mixed success.\textsuperscript{*}

\textsuperscript{*}The theory for rare-earth ions is discussed in a sequence of 14 technical reports of Harry Diamond Laboratories published between October 1973 and February 1977, entitled Rare Earth Ion-Host Interactions.
In a number of cases it was pointed out that the next higher level must be taken into account (e.g., Ti$^{2+}$ in sect. 5), since the predicted crystal-field splitting is of the same order as the free-ion separation of the levels (in Ti$^{3+}$ the $3p_{3/2}$-3P spacing). In these cases the Coulomb interaction described by the Slater parameters $F(k)$ must be considered; these, generally, are obtained from the free-ion data where available.* The dependence of the $F(k)$ on a particular host crystal can be approximated by the theory developed elsewhere.\textsuperscript{19}

For the $nd^{N}$ ions in ionization states greater than 3, no values of $\langle r^N \rangle$ are available.\textsuperscript{17} Perhaps a method employing simple Slater orbitals, which have been used successfully in rare-earth ions,\textsuperscript{1} can be used to obtain usable estimates of $\langle r^N \rangle$. Recently, a more sophisticated approach to Slater orbitals has been published\textsuperscript{20} which may be applied to obtain more accurate values of $\langle r^N \rangle$.

The effect of including the spin-orbit interaction should be investigated more thoroughly, particularly for the ions in the $nd^{N}$ series for $N > 5$. In general for $N > 5$, the spin-orbit constant becomes quite large, and the weak-field approximation should be augmented to include this interaction. That is, we assume that the crystal-field and spin-orbit interactions are approximately equal but both much less than the Coulomb interaction. Such an approximation is valid in the configurations with $N > 5$.

As we mentioned earlier, the point-charge model of crystal fields is very reliable for the fluoride host materials. Professor D. Gabbe of the Massachusetts Institute of Technology has made us aware of a number of fluoride garnets\textsuperscript{*} which have the same crystal structures as GSGG. These fluoride garnets are of the form $Na_3M_2Li_3F_{12}$, with $M = Sc$, In, or Rh and where

\footnotesize
\begin{itemize}
  \item[\textsuperscript{17}] S. Fraga, J. Karwowski, and K. M. S. Saxena, Physical Sciences Data, Vol. 5; Handbook of Atomic Data, Elsevier/North-Holland, New York (1976). [The values of $\langle r^N \rangle$ are not reported for ionization states greater than 3.]
  \item[\textsuperscript{19}] C. A. Morrison, Host Dependence of the Rare-Earth Ion Energy Separation $4f^{N-1}4f$ $n\ell$, J. Chem. Phys. 72 (1980), 1001.
  \item[\textsuperscript{20}] V. Maráz, Approximate Functions for 4s, 4p Slater-Orbitals for Transition Metal Ions having $d^{N}$ Electron Configurations, Acta Phys. Chem. 23 (1977), 225.
  \item[\textsuperscript{1}R. P. Leavitt and C. A. Morrison, Simple Model for the Energy Gap and its Variation with Pressure in Rare-Earth Monochalcogenides, Phys. Rev. B (manuscript in preparation).
  \item[\textsuperscript{2}We wish to thank Professor D. Gabbe of MIT for copies of a number of papers on fluorinated host materials, including J. Sugar and C. Corliss, Energy Levels of Vanadium, VI through VXXIII, J. Phys. Chem. Ref. Data 7 (1978), 1191.
\end{itemize}

19
the M site has $C_{3i}$ symmetry. It would be possible to dope a large number of
$Nd^{N}$ ions into the M site (16(a) site in space group No. 230, with $C_{3i}$
symmetry). The calculation of the crystal-field splitting in $C_{3i}$ symmetry is
partially complete and should not present a great deal of difficulty.

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1120.\]
LITERATURE CITED


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(17) S. Fraga, J. Karwowski, and K. M. S. Saxena, Physical Sciences Data, Vol. 5, Handbook of Atomic Data, Elsevier/North-Holland, New York (1976). [The values of \(<r^K>\) are not reported for ionization states greater than 3.]


(20) V. Maráz, Approximate Functions for 4s,4p Slater-Orbitals for Transition Metal Ions having d^N Electron Configurations, Acta Phys. Chem. 23 (1977), 225.

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