

scattering data would indicate KBr would be a very good substance for using in further investigations. If a monochromatized beam of x-rays were used the complicating factor due to the $\alpha_1\alpha_2$ radiations would be eliminated, at the expense of the intensity of the incident beam, however.

ACKNOWLEDGMENT

The author wishes to thank Professor William H. Zachariasen for his valuable aid and criticism throughout this investigation. We also wish to thank Mr. Paul C. Weyrich of the University of Michigan for the gift of the excellent artificial potassium chloride crystals.

FEBRUARY 1 AND 15, 1942

PHYSICAL REVIEW

VOLUME 61

First Spark Spectrum of Neodymium—Preliminary Classification and Zeeman Effect Data

WALTER E. ALBERTSON, GEORGE R. HARRISON, AND J. RAND McNALLY, JR.
*George Eastman Research Laboratories of Physics, Massachusetts Institute of Technology,
Cambridge, Massachusetts*

(Received November 29, 1941)

Classification by means of the combination principle of 367 lines of Nd II as arising from 30 lower and 57 upper levels has been checked by Zeeman effect measurements at fields up to 87,180 oersteds, and by other data from the M.I.T.-W.P.A. wave-length project. Quantum numbers have been assigned to those levels which have approximate LS coupling, and g values of all known levels have been determined. The lowest term is $4f^4(^5I)6s - a^4I$. All of the low terms found arise from $4f^46s$ and $4f^45d$, while all identified upper terms are believed to arise from $4f^46p$. The strongest lines in the spectrum belong to the sextet and quartet supermultiplets arising from the transition $4f^4(^5I)6p - 6s$, but these show perturbations which give rise to important intensity anomalies which affect the selection of *raies ultimes*. Curves are given which show the variation, in the progression La II, Ce II, Pr II, and Nd II, of the binding of terms arising from the configurations $f^n s$, $f^n p$, $f^n d$ and, where known, f^{n+1} .

NEODYMIUM ($Z=60$) is third in order of the 14 elements in the Periodic Table called the "rare earths." It gives rise to extremely complex spectra, the normal atom being characterized, according to the Bohr-Stoner theory, by six outer electrons of which several are f electrons. No previous known attempt at classification of any of the Nd spectra has met with success, and only by making extensive Zeeman effect studies at high magnetic fields, and by using new determinations of the wave-lengths of lines between 2000 and 11,000 Å from the neodymium arc, have we succeeded in determining the basic regularities in Nd II.

Some 2700 intense lines of neodymium are listed in the *M.I.T. Wavelength Tables*,¹ while the M.I.T.-W.P.A. card catalog contains a total of 6000 lines believed to arise from this element.

Most of these lines can readily be ascribed to the normal atom or the first or second stages of ionization, on the basis of King's² studies with the electric furnace. In the present paper 367 Nd II lines are classified as arising from 30 lower and 57 upper levels, to the majority of which quantum numbers have been assigned. Zeeman effect data are included for such of the lines as show resolvable patterns at fields up to 87,180 oersteds. These data suffice to determine the Landé splitting-factors (g values) of all terms.

The only Zeeman determinations on Nd lines which we were able to find in the literature were those of Van de Vliet,³ who reported the separations of a large number of unresolved triplets and resolved patterns for 16 Nd II lines. Van de Vliet used magnetic fields of 38,500 oersteds. Since we had available fields more than twice as strong in

¹ *M.I.T. Wavelength Tables* (John Wiley & Sons, New York, 1939).

² A. S. King, *Astrophys. J.* **78**, 9 (1933).

³ H. J. Van de Vliet, Thesis Amsterdam (1939).

as column 5. The last two columns contain g values for the lower and upper levels, respectively, as calculated from the observed data. Lines for which no Zeeman data are entered were too weak to observe, or produced incompletely resolved or badly overlapped patterns. Values enclosed in parentheses were assumed from final averages for the level involved, and were then used to calculate a g value for the other level producing the line.

The levels found in the classification are listed in Table II. The first column lists the electron which, added to the configuration $4f^4(^5I)$ of Nd III, is believed responsible for the levels the designations of which are given in column 2, and value in cm^{-1} in column 3. In that part of the table containing the middle odd terms configuration assignments are not given, and in cases where exact term assignments are not known only the inner quantum number J is given. The columns headed g values contain respectively the theoretical g values for LS coupling and the g values observed. The final column gives the number of resolved patterns used in arriving at the average measured value of g given in the preceding column.

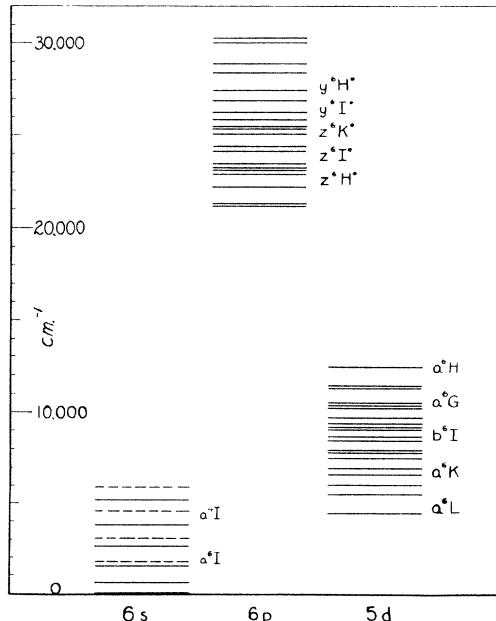


FIG. 1. Identified levels in Nd II to which complete quantum assignments have been made. The strongest lines in the spectrum are those arising from transitions between the upper group of levels and the two lower groups.

LOW CONFIGURATIONS OF SINGLY IONIZED NEODYMIUM

The neutral neodymium atom contains 60 electrons, of which 54 are in closed shells, while 6 are expected to be in the $4f$, $5d$, $6s$, and $6p$ shells. Following the normal order of binding, one might expect the lowest configuration of Nd I to be $4f^45d6s^2$, leading perhaps to a normal configuration in Nd II of $4f^35d6s^2$, $4f^46s^2$, or $4f^35d6s$. Instead, the trend observed in Ce II⁸ and Pr II⁹ is found to continue and $4f^46s$ is lowest, with $4f^55d$ only slightly higher, both combining strongly with $4f^46p$. The terms expected from these configurations are as follows:

$$\begin{aligned} f^4S &: {}^{6,4}(SDFGI) \quad {}^{4,2}(P_3D_2F_4G_3H_4L_2K_2LM) \\ &\quad {}^2(S_2D_4FG_4H_2I_3KL_2N) \\ f^4p &: {}^{6,4}(P_2D_2F_3G_2H_2IK) \\ &\quad {}^{4,2}(S_3P_5D_9F_9G_{11}H_9I_8K_5L_4M_2N) \\ &\quad {}^2(P_6D_5F_9G_7H_9I_6K_6L_3M_3NO) \\ f^4d &: {}^{6,4}(SP_2D_4F_3G_4H_3I_2KL) \\ &\quad {}^{4,2}(S_5P_9D_{12}F_9G_{11}H_{11}I_8K_6L_6M_4N_2O) \\ &\quad {}^2(S_4P_5D_{11}F_{11}G_{14}H_{11}I_{12}K_8L_7M_4N_3OQ). \end{aligned}$$

A diagram showing the energy levels of Nd II completely identified thus far is given in Fig. 1. All the low even terms found originate from the $4f^4(^5I)$ term of Nd III by addition of an s or a d electron, while most, if not all, of the upper terms found are believed to rise from addition of a p electron to the same parent configuration.

Table III gives the wave-lengths, estimated arc intensities and temperature classes of identified lines of the fundamental enlarged $s-p$ supermultiplet. Most of the lines in this array check within a few hundredths of a wave number with their calculated values, testifying to the validity of the assignments and the consistency of the wave-length determinations.

The *raies ultimes* of neodymium are usually given as 4303.573A, 3951.154A, and 4177.321A in decreasing intensity. We classify these lines as $a^6I_{3\frac{1}{2}} - z^6K_{4\frac{1}{2}}$, $a^6I_{5\frac{1}{2}} - 21^{\circ}_{5\frac{1}{2}}$, and $a^6I_{4\frac{1}{2}} - z^6K_{9\frac{1}{2}}$. One would expect $a^6I_{8\frac{1}{2}} - z^6K_{9\frac{1}{2}}$ to be the strongest line in the spectrum and hence the true *raie ultime*,

⁸ N. Rosen, G. R. Harrison, and J. R. McNally, Jr., Phys. Rev. **60**, 722 (1941).

TABLE III. Principal supermultiplet of Nd II, (incomplete).*

	$a^6I_{8\frac{1}{2}}$	$a^6I_{7\frac{1}{2}}$	$a^6I_{6\frac{1}{2}}$	$a^6I_{5\frac{1}{2}}$	$a^6I_{4\frac{1}{2}}$	$a^6I_{3\frac{1}{2}}$	$a^4I_{7\frac{1}{2}}$	$a^4I_{6\frac{1}{2}}$	$a^4I_{5\frac{1}{2}}$	$a^4I_{4\frac{1}{2}}$
$z^6K^o_{9\frac{1}{2}}$	4012.250 80 III	x	x	x	x	x	x	x	x	x
$z^6K^o_{8\frac{1}{2}}$	4284.518 25 IV	4061.085 40 III	x	x	x	x	4456.394 20 IV	x	x	x
$z^6K^o_{7\frac{1}{2}}$	—	4325.766 100 IV	4109.455 30 III	x	x	x	—	4462.985 60 IV	x	x
$z^6K^o_{6\frac{1}{2}}$	x	4602.242 10 V	4358.169 50 III	4156.083 10 III	x	x	—	—	4451.566 100 III	x
$z^6K^o_{5\frac{1}{2}}$	x	x	—	4351.295 30 III	4177.321 15 III	x	x	—	4676.262 2	4385.663 40 III
$z^6K^o_{4\frac{1}{2}}$	x	x	x	—	4400.828 50 III	4303.573 100 III	x	x	4958.139 5 V	4632.688 12 V
$y^6I^o_{8\frac{1}{2}}$	3973.269 40 IV	3780.391 20d IV	x	x	x	x	4120.654 6 IV	x	x	x
$y^6I^o_{7\frac{1}{2}}$	4205.595 20 IV	3996.100 40 IV	3805.359 50 III	x	x	x	4371.069 10	4106.582 25 IV	x	x
$y^6I^o_{6\frac{1}{2}}$	x	4227.719 20 IV	4020.872 15 III	3848.233 10d IV	x	x	—	4358.699 15 IV	4100.240 10 IV	x
$y^6I^o_{5\frac{1}{2}}$	x	x	4220.258 10d IV	4030.470 20 IV	3880.779 30 IV	x	x	—	4307.778 5 IV	4059.961 20 IV
$y^6I^o_{4\frac{1}{2}}$	x	x	x	4179.585 10 IV	4018.826 15 IV	3937.826 20 IV	x	x	—	4211.286 30 IV
$y^6I^o_{3\frac{1}{2}}$	x	x	x	x	4075.272 12 IV	3991.743 60 III	x	x	x	—
$z^6H^o_{8\frac{1}{2}}$	x	x	4859.030 60 IV	4609.230 5d	4414.432 12 IV	x	x	5361.174 3 V	—	4647.759 8 IV
$z^6H^o_{4\frac{1}{2}}$	x	x	x	4825.482 100 IV	4612.473 12 IV	4505.741 8	x	x	5228.427 6 V	4867.839 6 V
$z^6H^o_{3\frac{1}{2}}$	x	x	x	x	4811.343 60 IV	—	x	x	x	5089.837 10 IV
$z^6H^o_{2\frac{1}{2}}$	x	x	x	x	x	4706.542 50 IV	x	x	x	x

* x indicates line forbidden by selection principle for J ; lines not found are indicated by —

but this line, at 4012.250 Å, though given in our list at intensity 80 and stronger than the two weaker *raies ultimes*, is not usually included in lists of sensitive lines. Intensity anomalies which are similar in character to those found in Pr II⁹ will be noted in Table III. The whole matter of the most sensitive lines of Nd and Pr needs re-examination, and exact intensity measurements on these important lines would be well worth making.

Figure 2 shows the shift in binding of levels originating from the configurations $f^n s$, $f^n p$, and $f^n d$ for the progression La II, Ce II, Pr II, and

Nd II; and from f^{n+1} for the first two elements. The lowest $f^n s$ level is taken as zero in each case. This appears to be the actual lowest level of the spectrum except in the case of La II¹⁰ where Russell and Meggers find $5d^2$ and $5d6s$ levels still lower.

No attempt has been made to locate accurately the centers of gravity of the configurations in Fig. 2, but it is obvious that the differences $p-s$ and $p-d$ remain approximately constant through-

¹⁰ H. N. Russell and W. F. Meggers, Bur. Stand. J. Research 9, 625 (1932).

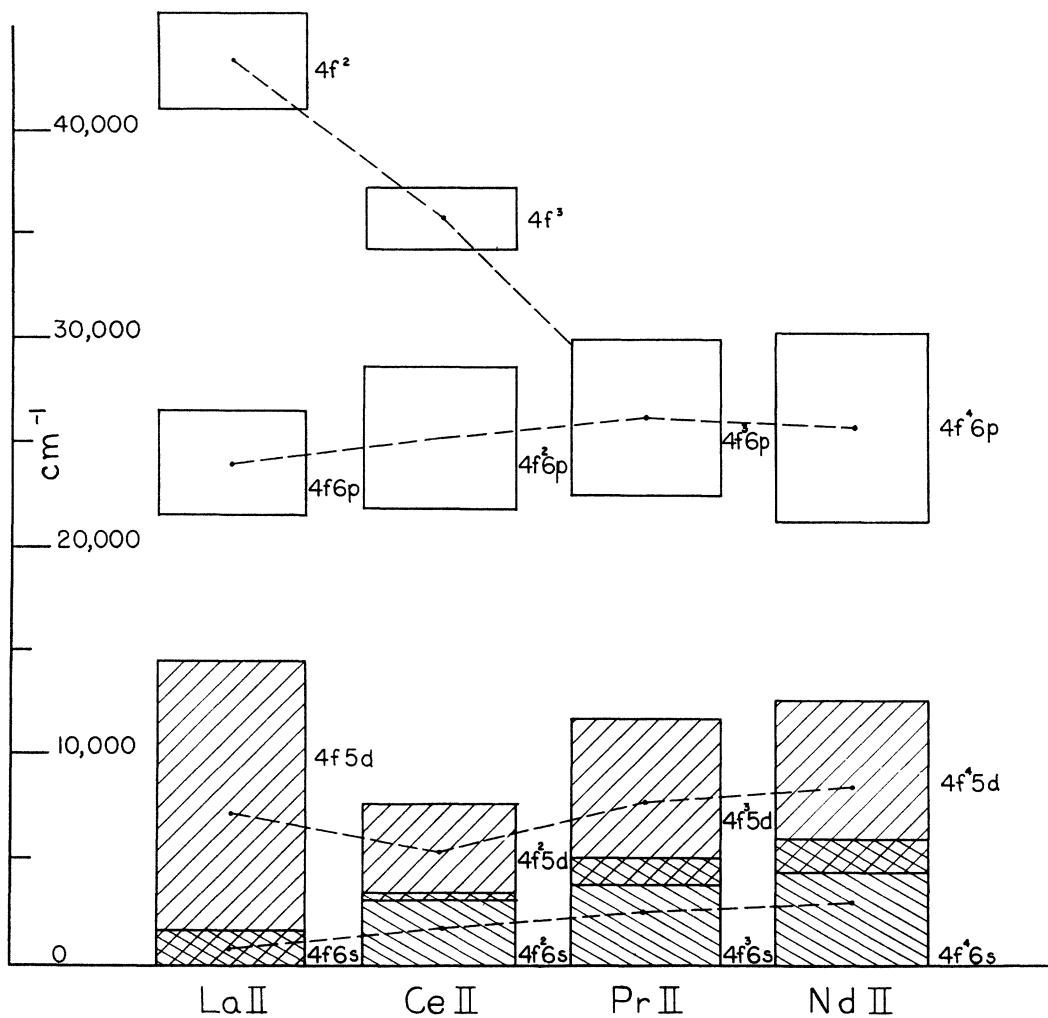


FIG. 2. Variation in the positions of levels due to homologous configurations through the progression La II, Ce II, Pr II, and Nd II, with the lowest level of $f^n s$ set at zero.

out the progression. The f^{n+1} configuration, on the other hand, becomes more closely bound in Ce II than in La II, and it appears that in Pr II many f^4 terms will be found in about the same location as the $f^3 p$ terms, while in Nd II they may lie even lower. Figure 2 shows clearly the origin of the great wealth of strong lines emitted by the four elements in and near the violet.

We desire to acknowledge the able assistance of clerical workers on the M.I.T.-W.P.A. Wave-

length Project in obtaining the basic data for this analysis, and to express appreciation of a grant from the Rumford Committee of the American Academy of Arts and Sciences in support of the work.

Note added in proof: In every case in this paper the designations $y^6 I^o_5$ and 21^o_5 should be interchanged. This applies to Tables I, II, and III, and simplifies the explanation of the *raies ultimes* anomaly.