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THE CRYSTAL SPECTRUM OF PROMETHIUM 3+ IN $LaCl_3$

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ABSTRACT

The absorption spectrum of Pm^{3+} in $LaCl_3$ was measured between 12,000 and 28,000 cm^{-1} for both sigma and pi polarizations. Free ion crystal field energy level calculations were made and the line groups $^5F_1$, $^5F_2$, $^5F_3$, $^5S_2$, $^5F_4$, $^5F_5$, $^3K_6$, $^5G_3$ and $^5G_2$ identified. Crystal field parameters were determined from the energy splittings in the first four line groups. Their values are $B_0^2 = 145$ cm^{-1}, $B_0^4 = -320$ cm^{-1}, $B_0^6 = -650$ cm^{-1}, and $B_6^6 = 450$ cm^{-1}. For these groups the exact free ion energy levels were calculated and the free ion parameters determined. Their values are $F_2 = 412.5$ cm^{-1}, $F_4 = 31.6$ cm^{-1}, $F_6 = 7.6$ cm^{-1}, and $\zeta = 977$ cm^{-1}.

I. INTRODUCTION

Triply ionized promethium is the last of the lanthanide ions to be investigated spectroscopically in a crystalline medium. The lowest spectroscopic term is ^5I. Earlier studies have examined the ion spectrum in a liquid, and the luminescence and fluorescence spectra in a crystal. We have extended the investigation to absorption in $LaCl_3$.

The first absorption spectrum of Pm 3+, other than the general structure, was obtained and reported by Gruber and Conway.[1] They measured the spectrum in solutions of D_2O and DCℓ from 2600 to 19,000 Å; they observed twenty-nine peaks, with the longest wavelength one at 8233 Å. They concluded that the ground state multiplets $^5I_4$ to $^5I_8$ should be separated by less than 5400 cm^{-1}, and that the groups of peaks around 8000 Å were probably due to transitions from $^5I_4$ to the ^5F and ^5S multiplets.

The same authors observed the luminescence spectrum of $PmCl_3$.[2] They prepared two crystals, one of 2% $PmCl_3$ in $LaCl_3$ and the other of 0.2% concentration. They found 34 lines of promethium luminescence, in seven groupings from 4610 to 8300 Å. They interpreted these as transitions from excited levels to the ground-state multiplet ^5I. Fluorescence was also observed when the crystals were irradiated with ultraviolet light; in the 2% crystal the multiplet at 8300 Å was intensified by a factor 10 after irradiation, as compared with self-luminescence, while the visible radiation was not notably enhanced. In the 0.2% crystal, all lines were intensified by ultraviolet irradiation of the crystal.

Interpretations of the solution spectra were given by Crozier and Runciman,[3] and by Hüfner.[4] These authors calculated the spin-orbit matrices

for f^4, and applied the results to Pm 3+. Crozier and Runciman noted that "since the solid-state results presently available are rather limited, no reliable correlation of calculated and experimental energy levels was possible". The paramagnetic resonance absorption of Pm 3+ in lanthanum ethyl sulfate was observed by Stapleton, Jeffries, and Shirley.[5] They were able to find a satisfactory spin Hamiltonian description, and deduced a value of g_{11} which was calculated with the use of average crystal field parameters for neighboring ions.

The solution spectrum was measured by Carnall, Fields, and Rajnak[6] for the purpose of comparing observed and calculated oscillator strengths. They also calculated the free-ion energy level scheme of Pm 3+ (and other trivalent lanthanides).[7]

The need for the crystal spectrum of the ion has also been emphasized by Dieke.[8] We present in this paper the crystal spectrum of Pm 3+ in $LaCl_3$ together with the results of analytic calculations for the identification of energy levels.

II. EXPERIMENTAL DETAILS

A $LaCl_3$ crystal doped with 0.1% of Pm was prepared for the experiment. About 5 mg of Pm_2O_3 was added to 2 gm of anhydrous $LaCl_3$, the mixture heated under vacuum, and the sublimate melted into a crystal growing tube. The tube was inserted into a furnace, heated to 900°C, and slowly lowered from the hot region. The result was a crystal 4 mm in diameter and 20 mm long. As before,[2] the crystal was self-luminescent, and it fluoresced when irradiated with ultraviolet light. It also gradually blackened, but its structure was not destroyed

as reported by Dieke.[8] The darkening could be removed by irradiation with light. Its behavior after 18 months remains substantially the same.

Absorption spectrograms were taken with a Jarrell-Ash 3.4 m plane grating spectrograph in the first, second, and eighth orders with plate factors of 44, 22, and 5.5 cm^{-1}/mm respectively, at a wavenumber of 21,000 cm^{-1}. The continuous wavelength light source was a GE Quartzline lamp. The crystal was immersed in liquid helium and kept at a temperature of 4.2 K. A Glan-Thompson prism was placed before the spectrograph slit to separate the two polarizations. Exposure times ranged from 4 m to 1 h on Eastman Kodak Spectrographic Plates types I-0, 103aF, and I-N. Wavelengths from an iron arc were used as standards.

The spectrograms were measured on a Grant semi-automatic comparator and the data reduced by digital computer. The relative intensities were visually estimated from plates and from the oscilloscope traces on the comparator.

The results are presented in Table I, and represent averages taken from several spectrograms at each wavelength. Lines strong in one polarization sometimes appear in the orthogonal polarization, but this is the effect of a slight and unavoidable misalignment between the crystal and polarizer axes.

Several checks were made to insure that the spectrum was free from impurities. A spark spectrum analysis of the original Pm_2O_3 sample showed it to be free of Sm to at least one part in 500. A separate crystal of $LaCl_3$ was grown, and its spectrum examined; no impurity lines were found. Finally, the data were scanned for the strongest lines of neighboring rare earths Nd and Sm; again no impurity lines were found.

III. ANALYSIS

We started analysis bh identifying transitions from the $^5I_4$ ground state to the low-lying ^5S and ^5F levels. To do this we needed estimates of the radial parameters; first we fitted the solution spectrum data of Gruber and Conway[1,2] to theoretical free ion energy level calculations. Then we made an alternative estimate by interpolating between values found from crystal spectra of other rare earths; we adopted the averages values $F_2 = 344.3$, $F_4 = 50.2$, $F_6 = 5.5$, and $\zeta = 1059.3$ cm^{-1}. The positions of all the terms belonging to the electron configuration f^4 were then calculated by the usual methods.[8] An examination of the spectrum immediately led to the identification of groups of lines in the 12,000 cm^{-1} to 16,000 cm^{-1} region as transitions from the $^5F_1$, $^5F_2$, $^5F_3$, $^5S_2$, $^5F_4$, and $^5F_5$ free ion levels split by the crystal field. The calculation indicated that the $^3K_6$ was the only multiplet at 16890 cm^{-1}. The two multiplets at 18020 and 18143 cm^{-1} were in good agreement with the calculation and they agree with the intensity estimates using the $U^{(\lambda)}$ matrix elements of Carnell <u>et al</u>.[7] They are assigned as $^5G_3$ and $^5G_2$ respectively. The J = 4 calculates in the region of 17800 but is very badly mixed. It could be assigned to the 17900 group solely on the basis of this fit. Nothing calculates near the 17450 group. The J = 7 tends to calculate above 18000 cm^{-1}. The J = 8 calculates at 19530 and is probably the first J value of the group of lines starting at 19725 cm^{-1}. However, if these last two assignments are made the resulting fit is not good. Groups from higher levels could not be identified because the increased mixing of states and the decreased spacing between levels made the line groups intermingle and the approximations less reliable.

Next we made more detailed comparisons with calculations from crystal field splittings, using expressions given in Wybourne.[10] We derived trial values for the crystal field parameters by interpolation from other rare earth ions. Identification proved easy; we then adjusted the trial values of the parameters with a least-square fitting procedure[11] which gave us an rms deviation of 2.75 cm^{-1}. Thirteen components of $^5I_4$ and $^5F_{1,2,3}$ were used to derive the following values: $B_0^2 = 145$, $B_0^4 = -320$, $B_0^6 = -650$, and $B_6^6 = 450$ cm^{-1}. A comparison between the theoretical and empirical energy levels is shown in Fig. 1.

From the positions of the free ion levels several attempts were made to obtain improvement to the existing free ion parameters. Using ten levels in a fitting calculation an rms deviation of 33 cm^{-1} was obtained. The parameters are $F_2 = 412.5$, $F_4 = 31.6$, $F_6 = 7.6$, and $\zeta = 977 \pm 8$ cm^{-1}.

It should be noted that the $^5S_2$ level is known not only for energy but also for S, L, and J; it shows no splitting in the crystal field. Therefore, any fit must yield the correct assignments for this level. When reasonable values for configuration mixing parameters were added to the fit, the deviation was much worse initially, and as the fit improved the composition of the $^5S_2$ level changed to $^5G_2$, an unacceptable result. Next we used different starting parameters, those of Carnall et al.[7] which had been derived from a fit to the Pm 3+ solution spectrum. For the same seven levels the rms deviation of the fit was 400 cm^{-1}. We varied F_2, F_4, F_6, and fixed the configuration parameters. As the fit improved the composition of $^5S_2$ again changed to that of $^5G_2$. An additional three levels predicted by both initial fits were then added to the calculation, but again as the fit improved the

composition of $^5S_2$ changed. Additional assignments which would agree with Carnall could be incorporated into the fit but this would not be any more meaningful. What is lacking is positive assignments to a sufficient number of upper levels. With such assignments the calculation would then remain within the bounds of the positively known data, and the assignments made by agreement with the predicted levels would have real meaning. Unfortunately, knowing the energy is not sufficient; positive identification of upper levels will have to be done with Zeeman effect experiments. The assignment of upper levels by means of agreement with calculations does not work in this case because slight variations in the electrostatic parameters cause states to cross each other. The assignments one makes to such levels vary, depending on the initial parameters and the whims of the programmer.

A comparison between the free ion parameter F_2 found for Pm 3+ and those of neighboring rare earth ions is shown in Fig. 2. The curve for zeta is shown in Fig. 3; it is smooth throughout. Numerical Hartree-Fock self-consistent-field wave functions for Pm 3+ and other rare-earth ions have been calculated by Saxena and Malli.[12,13] Their results for the energy of the 1s electrons is self-consistent to almost seven significant digits. However, their program puts special emphasis on the accuracy of the inner-electron distribution. Consequently the Hartree-Fock parameters which depend more on the outer-electron distribution have lesser numerical accuracies. The values for the Slater integrals are: $F_2 = 504\ cm^{-1}$, $F_4 = 66\ cm^{-1}$, and $F_6 = 8\ cm^{-1}$, which differ substantially from ours. For the spin-orbit parameter ζ they calculate $1070.85\ cm^{-1}$.

A plot of crystal field parameters B_0^2 is shown in Fig. 4a. Here, the comparisons show more deviations. The value for promethium falls on a smooth curve if we exclude neodymium. This fact is not reassuring; twenty multiplets were observed for Nd, while only five were observed for Sm, which seems to lie on a smooth curve.

The values of B_0^4 as given in Fig. 4b show fewer deviations; all except Sm seem to fall on the straight line of nearly constant value for the parameter.

The ratio B_0^6/B_6^6 plotted in Fig. 4e has been shown on theoretical grounds by Hutchinson and Wong[14] to be very nearly constant with a value 1.50. Our plot gives reasonable evidence of this, although the values of the parameters themselves plotted in Figs. 4c and 4d show considerable variations from smooth curves.

IV. CONCLUSION

Free ion and crystal field parameters have been obtained for Pm^{+3} in $LaCl_3$ which reproduce the observed low energy structure quite well. These parameters may be used as a starting point for an investigation of the higher energy structure.

It has been pointed out[8,14-16] that poor results in fitting higher levels may be expected. This difficulty is generally attributed to the unavailability of satisfactory free ion wave functions as well as sufficiently stringent selection rules. Hence, there is no guarantee that the least square fitting method will converge to meaningful assignments of energy levels.

We conclude that although further analysis within the framework of quamtum theory according to Racah should be attempted, a complete explanation

of the Pm^{+3} spectrum is unlikely until refinements in the theoretical techniques have been achieved and further experimental data are established.[17]

V. ACKNOWLEDGMENTS

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FOOTNOTES AND REFERENCES

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Table I. The Crystal Spectrum of the Promethium 3+ Ion in Lanthanum Tri-Chloride.

ENERGY IN cm^{-1}	MEASURED TRANSITIONS RELATIVE INTENSITY SIGMA	PI	APPROXIMATE LINE WIDTH cm^{-1}	ENERGY LEVEL TRANSITION ASSIGNMENT FREE ION QUANTUM NUMBERS LOWER	UPPER	CRYSTAL FIELD QUANTUM NUMBERS LOWER	UPPER
12,233.7		3	1.5			-3	±0
12,249.2	5	2	2.0			±2	±0
12,267.2	6	2	3.0	$^5I_4$	$^5F_1$	±1	±1
12,333.8		10	4.0	(12341 cm^{-1})		-2	±1
12,349.9	9	3	3.0			-2	±0
12,458.4	1	1	1.0				
12,643.5	3		2.0			-3	±1
12,658.1		5	2.0			-3	±2
12,671.0	3		2.0	$^5I_4$	$^5F_2$	±2	±1
12,691.2	8	2	3.0	(12779 cm^{-1})		±1	±1
12,704.3		8	3.0			±1	±2
12,726.9		4	2.0			±1	±0
12,757.4		4	1.5			-2	±1
12,770.6	4	1	2.0			-2	±2

(continued)

Table I. (continued)

ENERGY IN cm^{-1}	MEASURED TRANSITIONS RELATIVE INTENSITY SIGMA	PI	APPROXIMATE LINE WIDTH cm^{-1}	ENERGY LEVEL TRANSITION ASSIGNMENT FREE ION QUANTUM NUMBERS LOWER	UPPER	CRYSTAL FIELD QUANTUM NUMBERS LOWER	UPPER
12,811.0	8	3	4.0			-2	±2
13,396.6		1	1.0				
13,457.7	4	6	3.0				
13,484.8	4		3.0			-3	-3
13,506.8	6	2	2.0			-3	±0
13,517.7	6		2.0			±1	-3
13,522.1		1	1.0	$^5I_4$ (13614 cm^{-1})	$^5F_3$		
13,551.5		7	3.0			-3	±1
13,565.1	4		2.0				
13,585.2	6	1	2.0			-2	-3
13,588.6	7	2	2.0			±1	+3
13,606.8	7	2	2.0			-2	±0
13,650.6		8	3.0			-2	±1
14,100.7	2	2	2.0			-3	±1,±2

(continued)

Table I. (continued)

ENERGY IN cm^{-1}	MEASURED TRANSITIONS RELATIVE INTENSITY SIGMA	PI	APPROXIMATE LINE WIDTH cm^{-1}	ENERGY LEVEL TRANSITION ASSIGNMENT FREE ION QUANTUM NUMBERS LOWER	UPPER	CRYSTAL FIELD QUANTUM NUMBERS LOWER	UPPER
14,117.8	7	7	2.0	$^5I_4$	$^5S_2$	+2	±1,±2
14,135.3	8	8	2.0	(14200 cm^{-1})		±1	±1,±2
14,200.0	10	10	4.0			-2	±1,±2
14,404.1	4		2.0				
14,430.4	3		2.0				
14,455.9	4		2.0				
14,464.1		5	2.0				
14,478.7		8					
14,493.8	4		2.0				
14,508.9	3		2.0				
14,512.3	4		2.0				
14,516.2		8	3.5				
14,529.9	8	2	3.0	$^5I_4$	$^5F_4$		
14,560.9	4		2.0	(14530 cm^{-1})			
14,578.3	1	7	3.0				

(continued)

Table I. (continued)

ENERGY IN cm^{-1}	MEASURED TRANSITIONS RELATIVE INTENSITY SIGMA	PI	APPROXIMATE LINE WIDTH cm^{-1}	ENERGY LEVEL TRANSITION ASSIGNMENT FREE ION QUANTUM NUMBERS LOWER	UPPER	CRYSTAL FIELD QUANTUM NUMBERS LOWER	UPPER
14,582.2	6	1	2.0				
14,609.9	3	8	3.0				
15,801.9	1		1.5				
15,809.0	1		1.5				
15,868.2		5	3.0				
15,888.0	5	1	2.0	$^5I_4$ (15890 cm^{-1})	$^5F_5$		
15,894.8		6	2.0				
15,900.0		1	2.0				
15,908.8	6		2.0				
15,910.0		1	1.0				
15,912.8	1		1.0				
16,809.8	1		1.0				
16,820.8		1	1.0				
16,827.3	1		1.0				

(continued)

Table I. (continued)

ENERGY IN cm^{-1}	MEASURED TRANSITIONS RELATIVE INTENSITY SIGMA	PI	APPROXIMATE LINE WIDTH cm^{-1}	ENERGY LEVEL TRANSITION ASSIGNMENT FREE ION QUANTUM NUMBERS LOWER	UPPER	CRYSTAL FIELD QUANTUM NUMBERS LOWER	UPPER
16,836.4	1	2	1.0				
16,883.0	3		2.0				
16,887.5	4		2.0	$^5I_4$ (16890 cm^{-1})	$^3K_6$		
16,893.8	5	4	2.0				
16,903.1	4		2.0				
16,920.6		4	2.0				
16,926.9	1		1.0				
17,388.1	1		1.0				
17,415.5	6	2	5.0				
17,428.0	6		4.0				
17,437.8	5		3.0				
17,446.3	4		2.5				
17,449.1		5	5.0				
17,512.6	9	9	5.0				

(continued)

Table I. (continued)

ENERGY IN cm^{-1}	MEASURED TRANSITIONS RELATIVE INTENSITY SIGMA	PI	APPROXIMATE LINE WIDTH cm^{-1}	ENERGY LEVEL TRANSITION ASSIGNMENT FREE ION QUANTUM NUMBERS LOWER	UPPER	CRYSTAL FIELD QUANTUM NUMBERS LOWER	UPPER
17,515.6		2	1.0				
17,537.5	9	3	4.0				
17,703.7		1	2.0				
17,708.0		1	2.0				
17,723.0	1		2.0				
17,729.5		1	2.0				
17,763.8	3	3	2.0				
17,829.8	7	7	3.0				
17,903.0		4	4.0				
17,923.0	6		3.0				
17,963.0	4		2.5				
17,999.9	4		2.0				
18,029.0	10	9	5.0	$^5I_4$	$^5G_3$		
18,043.0		1	1.0	(18020 cm^{-1})			

(continued)

Table I. (continued)

ENERGY IN cm^{-1}	MEASURED TRANSITIONS RELATIVE INTENSITY SIGMA	PI	APPROXIMATE LINE WIDTH cm^{-1}	ENERGY LEVEL TRANSITION ASSIGNMENT FREE ION QUANTUM NUMBERS LOWER	UPPER	CRYSTAL FIELD QUANTUM NUMBERS LOWER	UPPER
18,057.4	3		2.5				
18,077.0	3		2.5				
18,084.4	3		2.5				
18,098.7	6		3.0				
18,143.5		9	4.0	$^5I_4$ (18143 cm^{-1})	$^5G_2$		
18,168.3	6		3.0				
18,170.5		3	1.0				
18,197.1		1	1.0				
18,254.0	3	1	2.0				
18,280.7	2		2.0				
18,287.8		2	2.0				
18,302.7	2		2.0				
19,725.3	3		2.0				
19,730.7	2	4	2.0				

(continued)

Table I. (continued)

ENERGY IN cm^{-1}	MEASURED TRANSITIONS RELATIVE INTENSITY SIGMA	PI	APPROXIMATE LINE WIDTH cm^{-1}	ENERGY IN cm^{-1}	MEASURED TRANSITIONS RELATIVE INTENSITY SIGMA	PI	APPROXIMATE LINE WIDTH cm^{-1}
19,792.4	4		2.5	21,096.9	3		2.0
19,807.3		4	2.5				
19,822.8	4		2.5	21,595.0	5		2.0
19,972.5	5		3.0	21,614.2	6	1	3.0
19,996.5		2	2.0	21,635.0	5		2.0
				21,660.4		4	3.0
20,018.5	3	5	3.0	21,674.0	4		2.0
20,037.9	1	8	4.0	21,680.0	8	2	3.0
20,061.4	2	7	4.0	21,691.0	3	9	3.0
20,082.8	3		3.0	21,727.5		3	2.0
20,116.4	3		2.0				
20,150.0	9	9	5.0	22,081.3		2	2.0
20,172.4	2		1.0	22,106.9		8	3.0
20,192.7	2		1.0	22,127.9	6		3.0
20,208.3	6	1	4.0	22,140.5		6	3.0
21,066.6		4	2.0	22,149.3	4		2.5

(continued)

Table I. (continued)

ENERGY IN cm^{-1}	MEASURED TRANSITIONS RELATIVE INTENSITY SIGMA	PI	APPROXIMATE LINE WIDTH cm^{-1}	ENERGY IN cm^{-1}	MEASURED TRANSITIONS RELATIVE INTENSITY SIGMA	PI	APPROXIMATE LINE WIDTH cm^{-1}
22,226.2		2	2.0	24,018.0	3	3	2.0
22,247.5	2		2.0				
22,396.7		2	2.0	24.401.5	3		2.0
				24,415.5	1		1.0
22,836.0	1	2	2.0				
				24,446.0	4		2.0
22,852.2	3		2.0				
				24,525.0	2		3.0
22,936.5	6	6	3.0				
				24,535.1		2	1.0
22,983.0	5		3.0				
				24,547.2		2	1.0
23,535.3		2	4.0	24,551.4	3		3.0
23,592.8	6		3.0	24,559.7		1	1.0
23,602.5	4		2.0	24,602.0	9		4.0
23,657.3	3		2.0	24,617.5		5	3.0
23,775.5	1		2.0	24,631.0	5		1.5
23,803.0	4	4	3.0	24,643.0	5		1.5
23,841.7		2	2.0	24,730.6		4	2.0

(continued)

Table I. (continued)

ENERGY IN cm^{-1}	MEASURED INTENSITY RELATIVE INTENSITY SIGMA	PI	APPROXIMATE LINE WIDTH cm^{-1}	ENERGY IN cm^{-1}	MEASURED INTENSITY RELATIVE INTENSITY SIGMA	PI	APPROXIMATE LINE WIDTH cm^{-1}
24,760.3	4		3.0	26,884.3	5		2.0
24,792.4	5		3.0	26,941.7	3		1.0
24,798.2		5	3.0	27,027.9	8		6.0
25,547.6	1		1.0	27,046.3		5	3.0
25,584.2		2	1.5	27,113.6	3		2.0
25,612.7	1		1.0	27,146.6	7		2.0
25,656.6	1		1.0	27,213.3		9	5.0
25,974.7	4		2.0	27,254.0	4	7	2.0
26,174.7		4	2.0	27,296.5		4	2.0
26,272.3	3	6	2.0	27,380.3	6		2.0
26,307.6	3	4	2.0	27,419.9	4		2.0
26,745.9	3	6	2.0	27,435.6		6	2.0
				27,452.5	4		2.0

FIGURE CAPTIONS

Fig. 1. Crystal field energy level splittings: a, free ion level; b, calculated levels; c, observed levels. All units are cm^{-1} except for the crystal field quantum numbers given between calculated and observed levels.

Fig. 2. Experimentally determined values of the Slater integral F_2. Values taken from Ref. 10.

Fig. 3. Experimentally determined values of the spin-orbit splitting parameter ζ. Values taken from Ref. 10.

Fig. 4. Experimentally determined values of crystal field parameters for lanthanide ions in $LaCl_3$. Values taken from Ref. 10. a, B_0^2; b, B_0^4; c, $-B_0^6$; d, B_6^6; e, $-B_0^6/B_6^6$, compared to a theoretical value of 1.50.

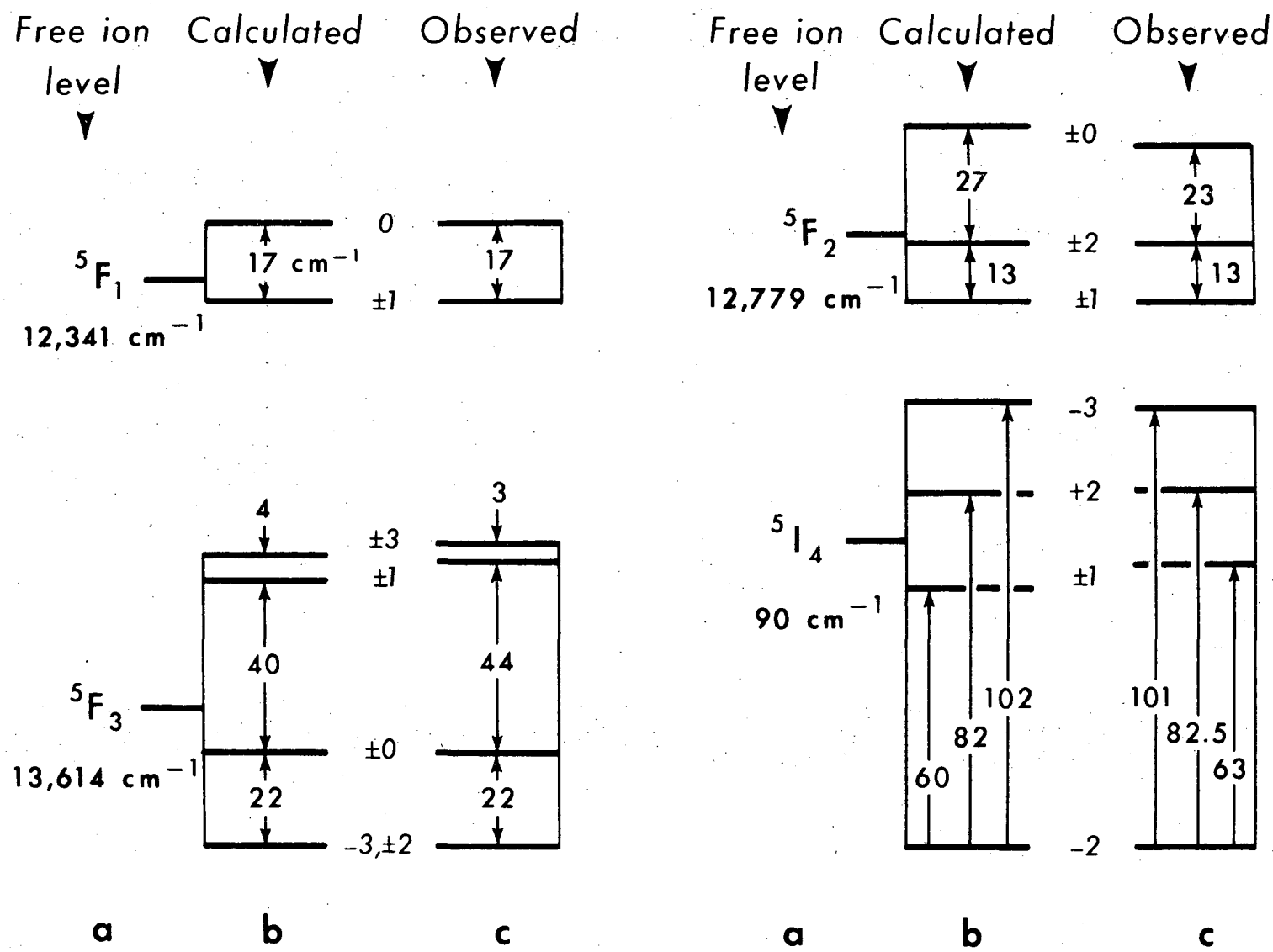
Free ion level
Calculated
Observed
$^5F_1$
12,341 cm^{-1}
17 cm^{-1}
0
±1
17
$^5F_3$
13,614 cm^{-1}
4
±3
±1
40
±0
22
-3,±2
3
44
22
a
b
c
Free ion level
Calculated
Observed
$^5F_2$
12,779 cm^{-1}
27
13
±0
±2
±1
23
13
$^5I_4$
90 cm^{-1}
-3
+2
±1
-2
60
82
102
101
82.5
63
a
b
c

Fig. 1

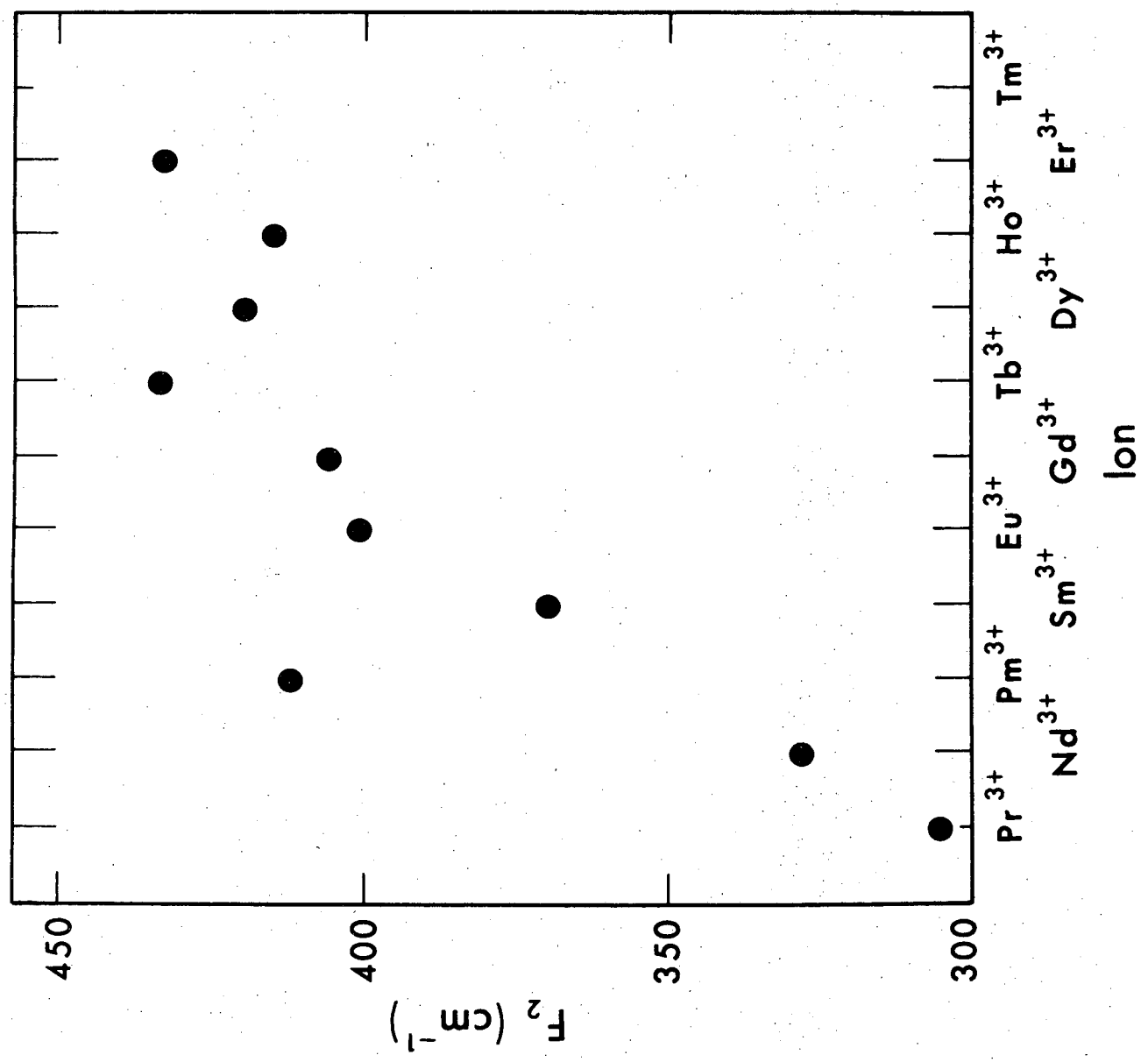
450
400
350
300
F_2 (cm^{-1})
Pr^{3+}
Nd^{3+}
Pm^{3+}
Sm^{3+}
Eu^{3+}
Gd^{3+}
Tb^{3+}
Dy^{3+}
Ho^{3+}
Er^{3+}
Tm^{3+}
Ion

Fig. 2

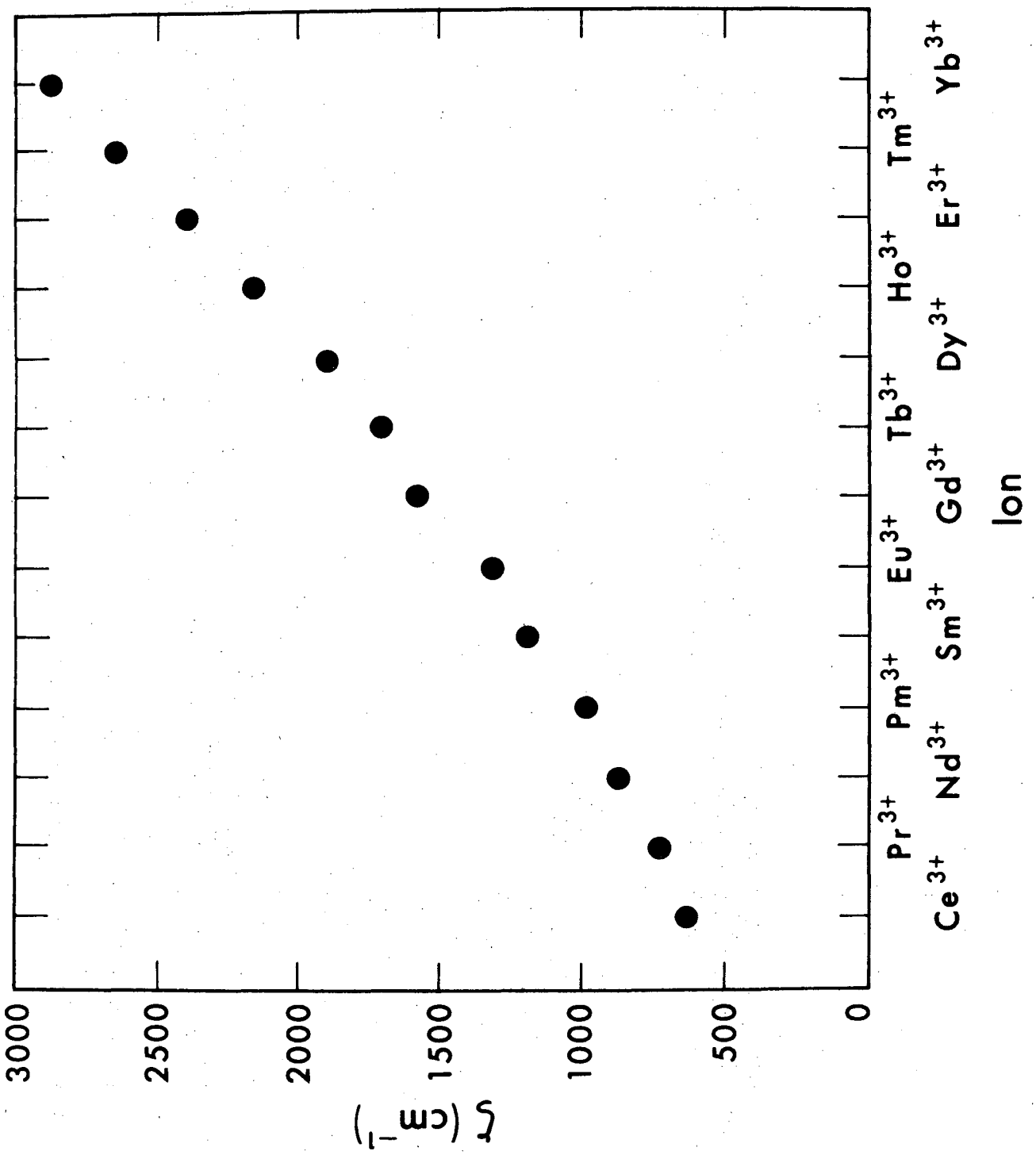
3000
2500
2000
1500
1000
500
0
ζ (cm⁻¹)
Ce3+
Pr3+
Nd3+
Pm3+
Sm3+
Eu3+
Gd3+
Tb3+
Dy3+
Ho3+
Er3+
Tm3+
Yb3+
Ion

Fig. 3

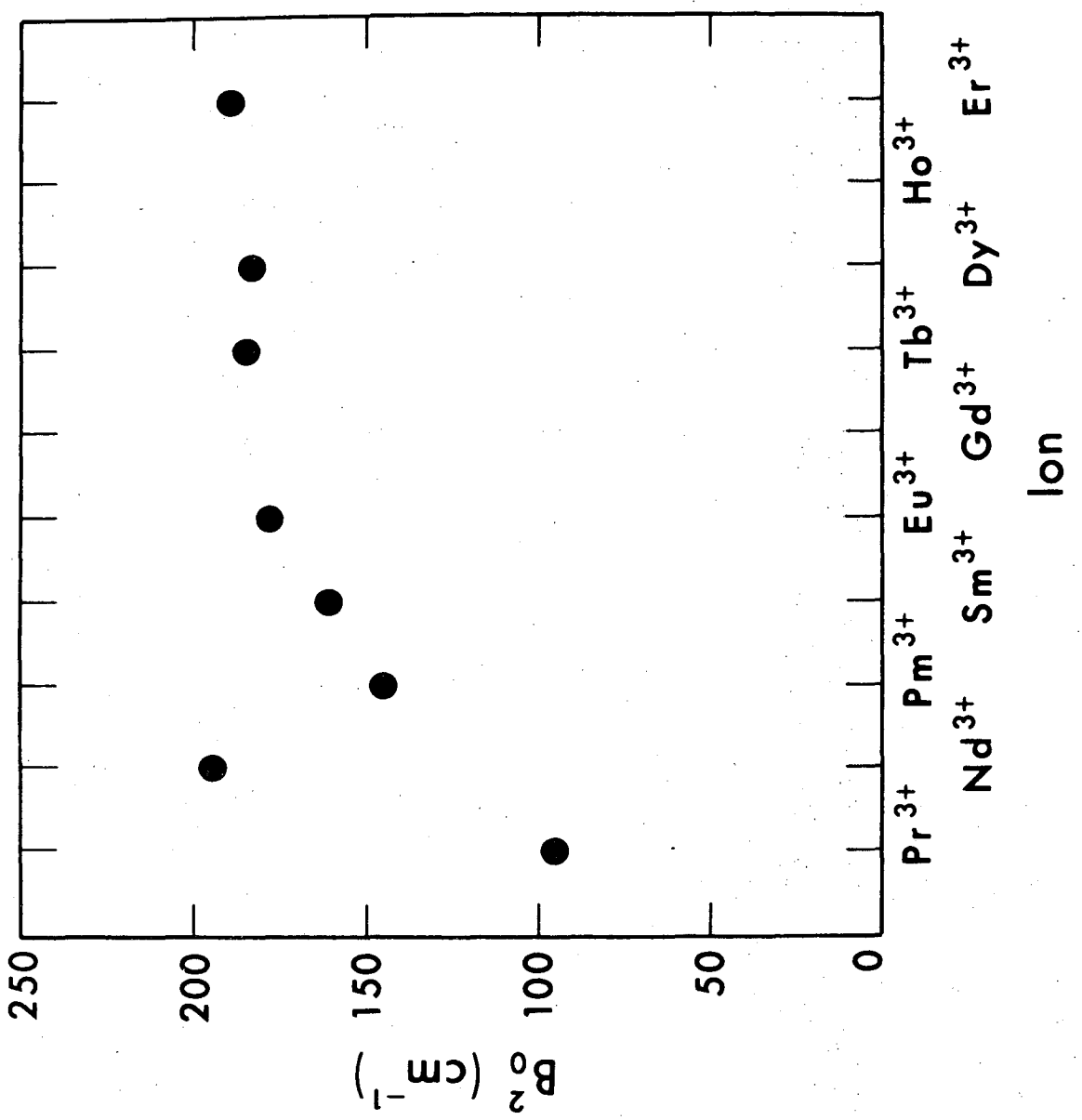
250
200
150
100
50
0
B_0^2 (cm^{-1})
Pr^{3+}
Nd^{3+}
Pm^{3+}
Sm^{3+}
Eu^{3+}
Gd^{3+}
Tb^{3+}
Dy^{3+}
Ho^{3+}
Er^{3+}
Ion

Fig. 4a

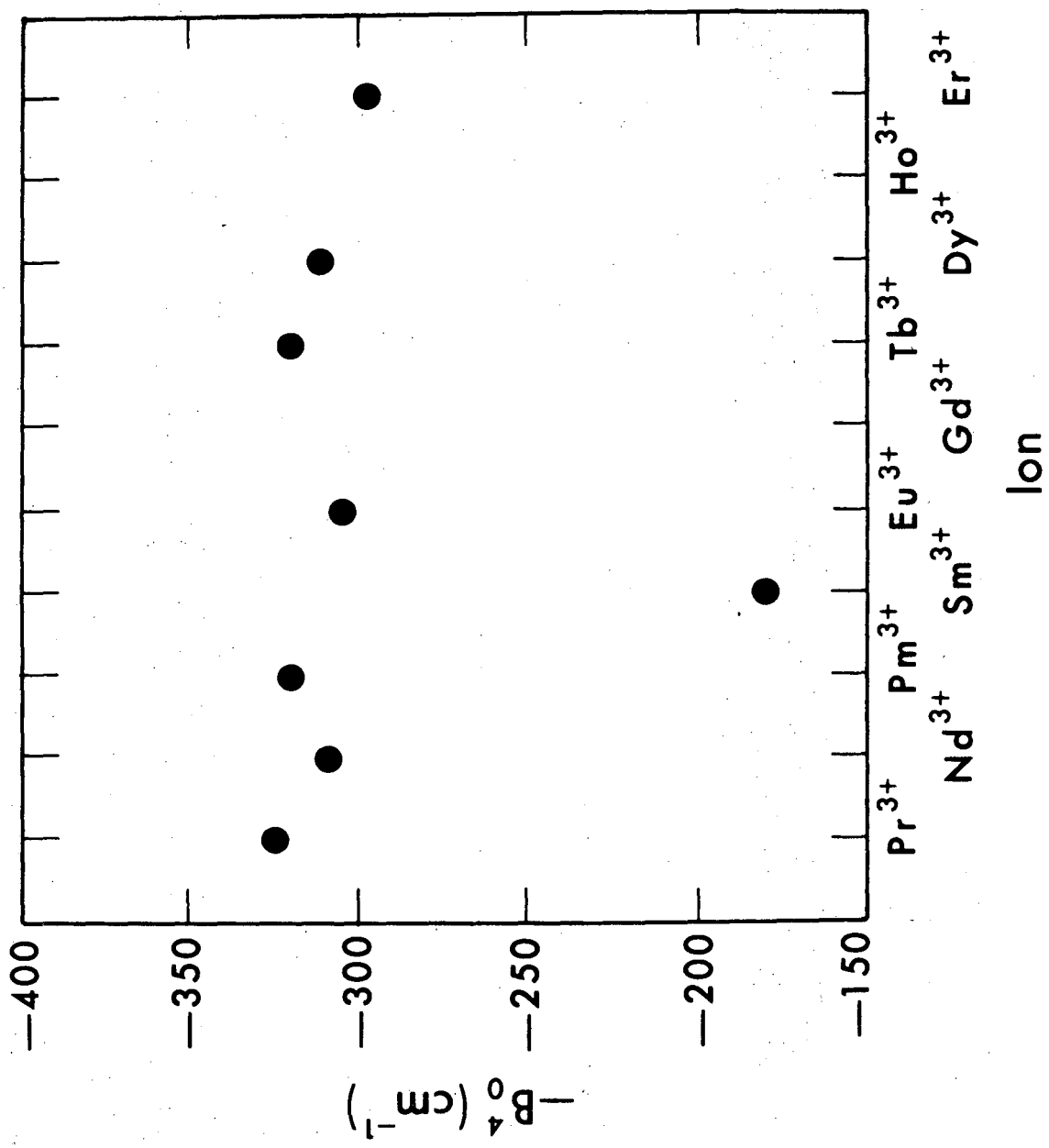
−400
−350
−300
−250
−200
−150
$-B_0^4$ (cm^{-1})
Pr^{3+}
Nd^{3+}
Pm^{3+}
Sm^{3+}
Eu^{3+}
Gd^{3+}
Tb^{3+}
Dy^{3+}
Ho^{3+}
Er^{3+}
Ion

Fig. 4b

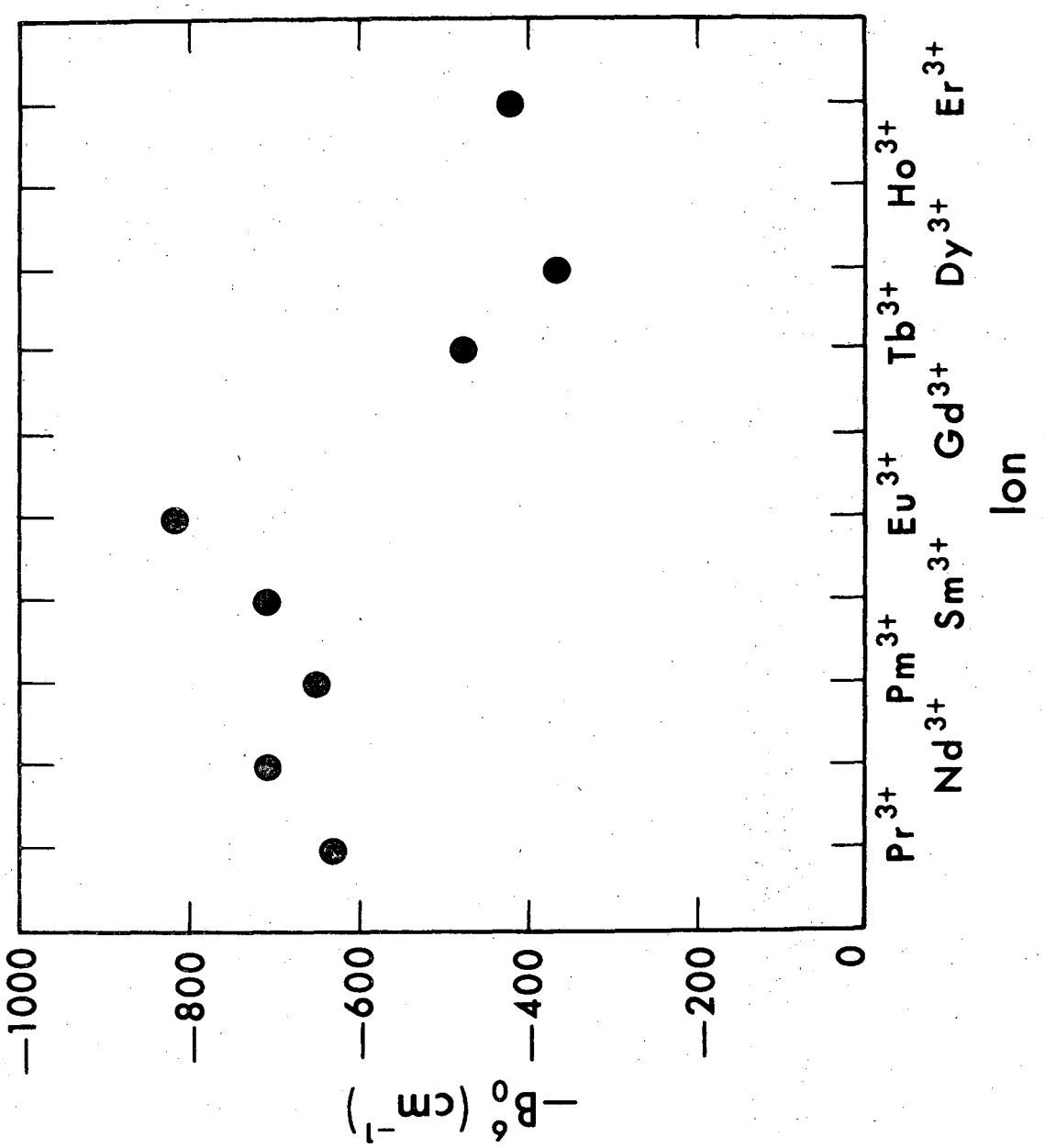
−1000
−800
−600
−400
−200
0
$-B_0^6$ (cm^{-1})
Pr^{3+}
Nd^{3+}
Pm^{3+}
Sm^{3+}
Eu^{3+}
Gd^{3+}
Tb^{3+}
Dy^{3+}
Ho^{3+}
Er^{3+}
Ion

Fig. 4c

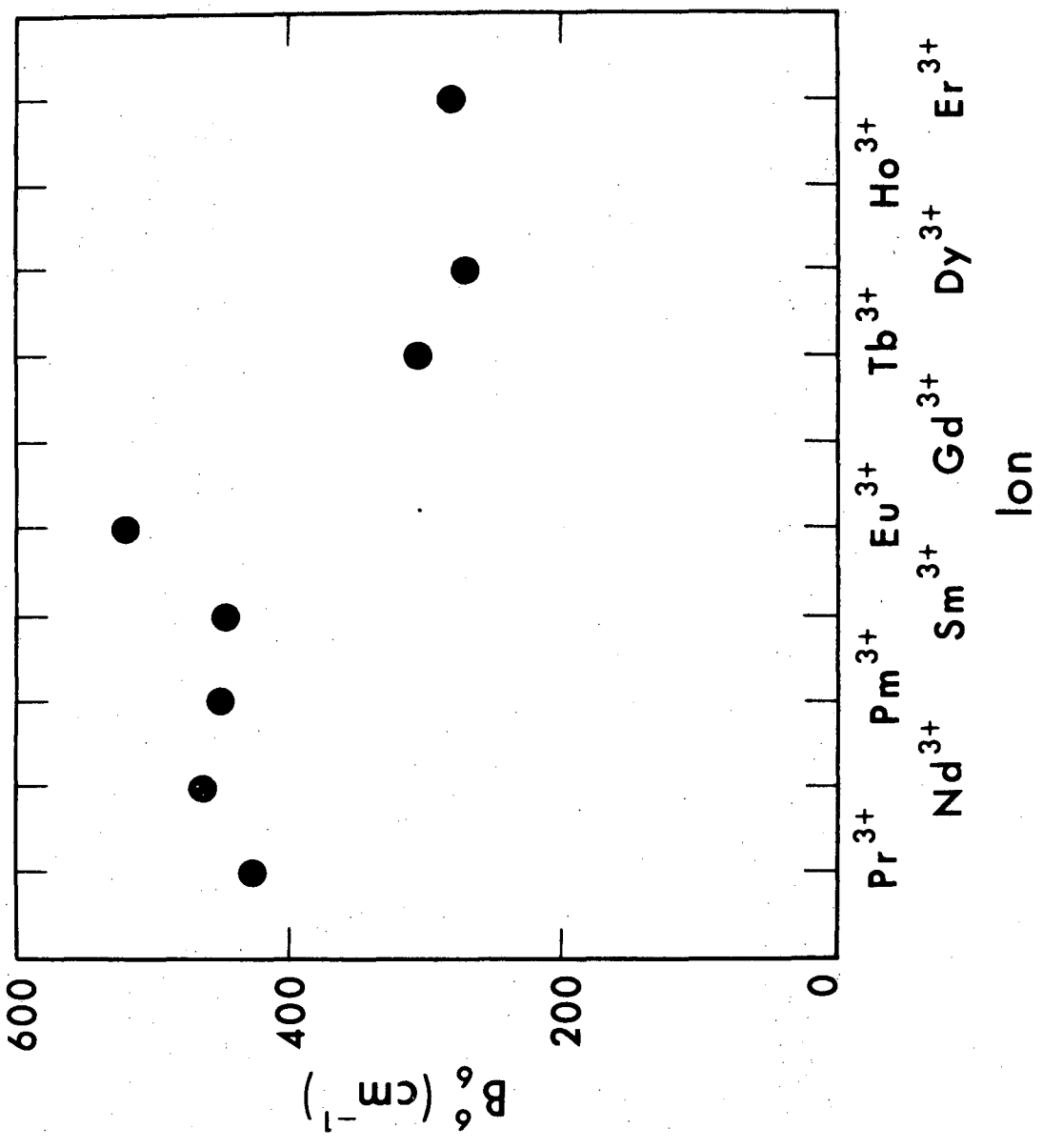

Fig. 4d

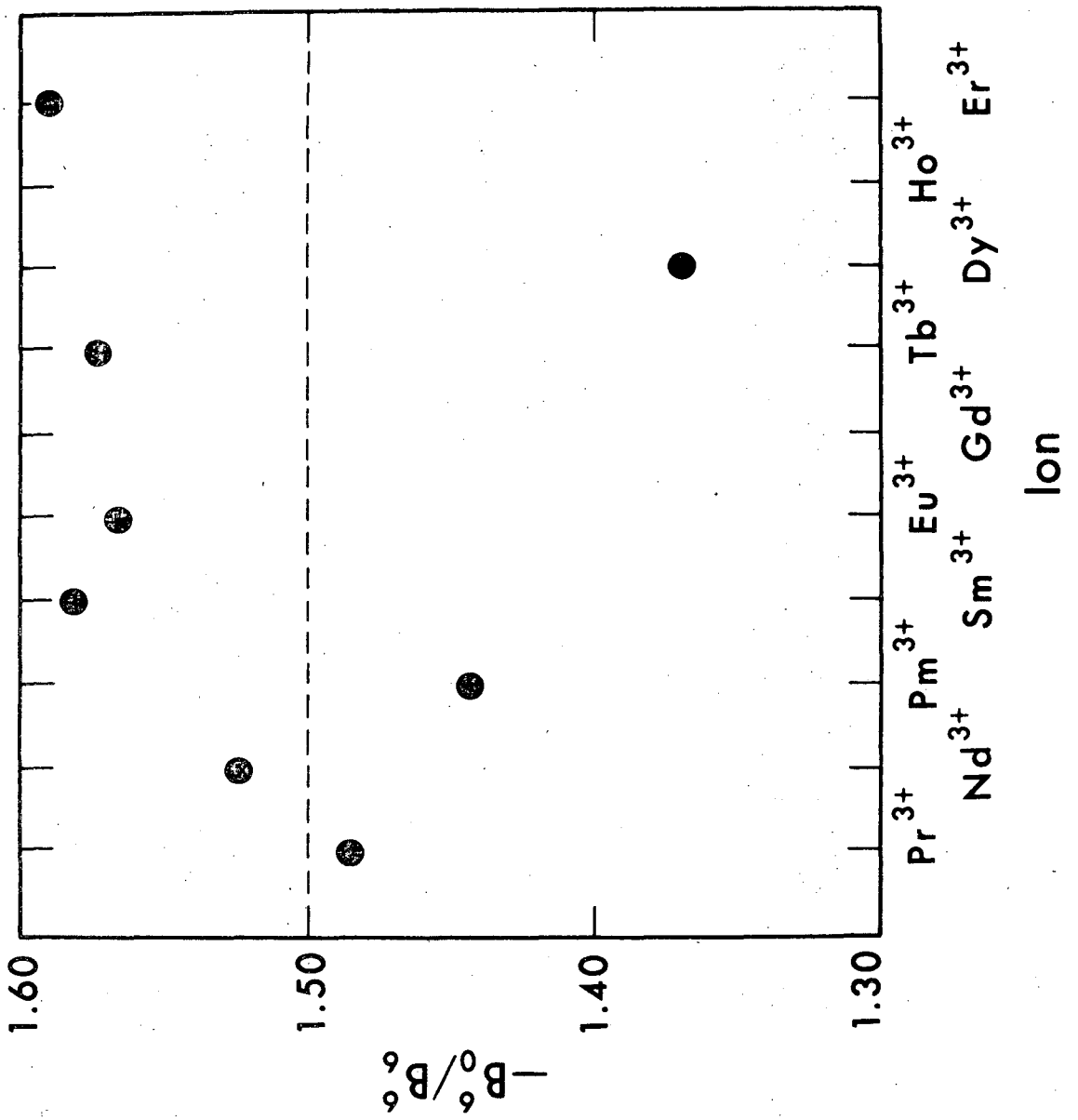
1.60
1.50
1.40
1.30
$-B_0^6/B_6^6$
Pr^{3+}
Nd^{3+}
Pm^{3+}
Sm^{3+}
Eu^{3+}
Gd^{3+}
Tb^{3+}
Dy^{3+}
Ho^{3+}
Er^{3+}
Ion

Fig. 4e

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