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Optical Absorption and Zeeman Spectra of Nd^{3+}-Doped $PbMoO_4$†

I. S. Minhas* and K. K. Sharma
Department of Physics, Indian Institute of Technology, Kanpur-16, India

John B. Gruber
Department of Physics, Washington State University, Pullman, Washington 99163

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The optical absorption and Zeeman spectra of $PbMoO_4$:Nd^{3+} single crystals containing Na^+ ions for charge compensation have been investigated between 5500 and 25 000 cm^{-1} at temperatures of 4.2, 77, and 300 °K. Polarization of the spectra has been helpful in identifying the crystalline Stark components of the $4f^3[SL]$ J levels of the Nd^{3+} ion. The experimental center of gravity for each of the 17 identified crystalline Stark-split J levels can be interpreted using the parameters $E^1 = 4924.2$, $E^2 = 24.3$, $E^3 = 471.7$, $\zeta_{4f} = 879.1$, $Y(22,1) = 3455$, and $Y(22,3) = -12\,020$ all in cm^{-1}. The parameters E^1, E^2, E^3, and ζ_{4f} are associated with the isolated configuration $4f^3$. The parameters $Y(22,1)$ and $Y(22,3)$ represent the dominant contributions from nonlinear configuration interactions. The simultaneous least-squares fitting that produced this best set of parameters yielded an rms deviation of 38 cm^{-1}. Inclusion of parameters α, β, and γ of the linear theory of configuration interaction did not improve the agreement. First-order crystal-field-splitting calculations were carried out involving a total of 54 different crystalline Stark levels. Assuming D_{2d} point-group symmetry for Nd^{3+} in the lattice, the best set of crystal-field-splitting parameters are $B_0^2 = 428.2$, $B_0^4 = -592.2$, $B_0^6 = -104.1$, $B_4^4 = -914.9$, and $B_4^6 = -691.8$ all in cm^{-1}. The rms deviation obtained was 13.7 cm^{-1}. Addition of the parameters $B_4^{'4}$ and $B_4^{'6}$ needed to describe a symmetry of S_4 recently reported for the ion in this crystal does not materially improve the agreement. Furthermore, Zeeman splittings calculated using the crystal-field-splitting wave functions based on D_{2d} symmetry agree rather well with the measured experimental values. The calculated and experimental Zeeman splitting for the ground crystalline Stark level is in agreement to within 0.7%.

I. INTRODUCTION

The optical-absorption, fluorescence, and Zeeman spectra of Nd^{3+} doped into various single-crystal host lattices have been the subject of research reported by a number of different investigators.[1-9] Single crystals of $PbMoO_4$ doped with Nd^{3+} have likewise received attention from several different groups.[10-12] The fluorescence and absorption spectra of several low-lying levels of the $PbMoO_4$: Nd^{3+} system were reported by Kariss and Feofilov.[10] An interpretation of these data was attempted by Shekun[11] and somewhat later by Sengupta *et al.*[12] However, the interpretations presented in these two different papers have limited value for the following reasons.

Shekun[11] included the effects of J-J mixing in his crystal-field-splitting calculations, but only in the Russell-Saunders approximation. Furthermore, he assumed a site symmetry of D_{2d} for the Nd^{3+} rather than the exact site symmetry of S_4. On the other hand, Sengupta *et al.*[12] did use intermediate coupling and made crystal-field-splitting calculations with and without J-J mixing based on the exact site symmetry S_4 for Nd^{3+}. However, because of the lack of experimental data, the values of E^1, E^2, E^3, and ζ_{4f} reported by Sengupta *et al.*[12] are questionable, and the effects of configuration interaction were ignored by them.

The purpose of this paper is to present additional experimental information which has allowed us to reexamine the previous interpretations and to present an improved analysis consistent with all the optical and magnetic data now available to us.

II. EXPERIMENTAL DETAILS

Single crystals of pure and doped $PbMoO_4$ were grown by the Czochralski method. Doping was carried out by adding 0.1-at.% Nd^{3+} to a stoichiometric mixture of PbO and MoO_3. The Nd^{3+} added was in the form of Nd_2O_3. The doped single crystals showed no spectroscopic evidence to indicate the presence of other rare-earth-ion impurities. In the doping process Nd^{3+} replaces or substitutes for a Pb^{2+} ion in $PbMoO_4$.[13,14] To handle charge compensation, we added between 0.1- and 0.4-at.% Na^+ as $Na_2MoO_4 \cdot 2H_2O$ to the melt. The crystals grown under these conditions are single and transparent. Our optical measurements indicate that Nd^{3+} is found predominantly in a single-site symmetry. To establish just how much Na^+ and Nd^{3+} were actually incorporated into our crystals during the growing process, we carried out a spectroscopic analysis of one of our crystals. We found Nd^{3+} and Na^+ concentrations to be on the order of 180 and 160 ppm, respectively.

The plane-polarized and -unpolarized optical spectra were recorded at 300, 77, and 4.2 °K using a Cary-14 spectrophotometer and a 3.4-m Ebert Jarrell-Ash spectrograph. The spectral range of the Cary-14 is between 3000 and 25 000 Å and the Jarrell-Ash spectrograph covers the range between 3000 and 10 000 Å. The average resolution of the Cary-14 over this spectral range is between 1 and 2 Å. For the Jarrell-Ash the resolution was better than 0.2 Å over the range covered. In terms of wave numbers, the spectra reported in this paper range between 5500 and 25 000 cm^{-1}. The Zeeman spectra were taken using a Magnion L-96 electromagnet having a capability of reaching 24 000 G, with a long-term stability of better than 0.01%. Measurements were made on samples with the magnetic field parallel to the crystallographic *c*-axis at liquid-helium temperature using the 3.4-m spectrograph. The Cary-14 spectra taken using a conduction Dewar filled with liquid helium are displayed in Figs. 1–3.

III. OBSERVED SPECTRA

The spectra, which consist of separated groups of lines, are generally stronger in π polarization than in σ polarization. The axial spectrum is similar to the σ-polarized spectrum indicating electric-dipole transitions are involved. The groups of observed lines can be placed roughly into two categories based on observed intensities. The strong group corresponds to transitions to excited levels that have substantial quartet ($S=\frac{3}{2}$) character and the weak group corresponds to transitions to excited levels that have primarily doublet ($S=\frac{1}{2}$) character. This appears consistent with the reasonably valid spin-selection rules $\Delta S=0$, $\Delta S\neq 1$, and where the $^4I_{9/2}$ ground level is almost a pure quartet state.

Some of the observed lines which are expected in σ polarization also show up in π polarization. However, the intensity in the allowed polarization (σ) of each line involved is much more than its intensity in the forbidden polarization (π). Similar effects have been reported in other systems.[14,15] Finally, in the Jarrell-Ash spectra, strong, sharp lines are sometimes accompanied by satellite lines (within a few cm^{-1}) on both sides. The characteristic features of these lines are very much similar to those reported by Prinz and Cohen[16] for Nd^{3+}-doped rare-earth chlorides. Some of the lines remain broad even at liquid-helium temperature. Perhaps this may be due to a dense satellite structure within the observed spectral envelope. In addition, several weak lines which are apparently unaffected by charge compensation appear in the neighborhood of the main lines. No detailed analysis of these lines was attempted here but it is not unreasonable to assume these lines are due to vibronic structure.

IV. IDENTIFICATION OF LEVELS

It is well known that 4*f* electrons of lanthanide ions interact rather weakly with their lattice environment. Consequently, the free-ion energy levels inferred from the crystal spectra show small energy shifts from host to host. However, the assignment of J values for Nd^{3+} in $PbMoO_4$ is a fairly simple matter except in cases where several J levels are found close in energy to one another. The identification is further facilitated by the polarization and Zeeman measurements and by the satellite structure effects.

For the system $PbMoO_4$: Nd^{3+}, a J level is expected to be split by the crystalline Stark field into $J+\frac{1}{2}$ doubly degenerate Stark components (some of which should appear only in σ and the others in both σ and π polarizations).[17] In the spectral range covered in our experiments the polarization characteristics and the number of Stark levels for most groups are in complete agreement with the free-ion-level assignments. The exceptions are the $J=\frac{11}{2}$ (III), $\frac{15}{2}$ (II), $\frac{9}{2}$ (V), and $\frac{3}{2}$ (III) levels.[18] The

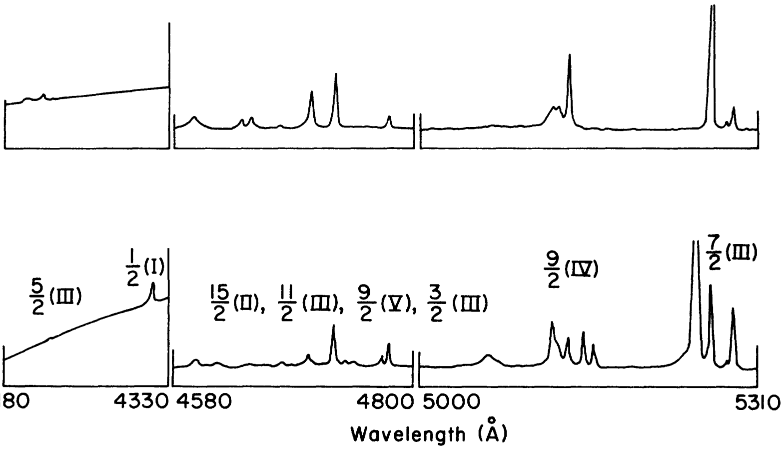

FIG. 1. Absorption spectra of $PbMoO_4$: Nd^{3+} taken between 4180 and 5310 Å using a conduction Dewar filled with liquid helium. The π-polarization spectrum is given on the top and the σ-polarization spectrum is presented on the bottom.

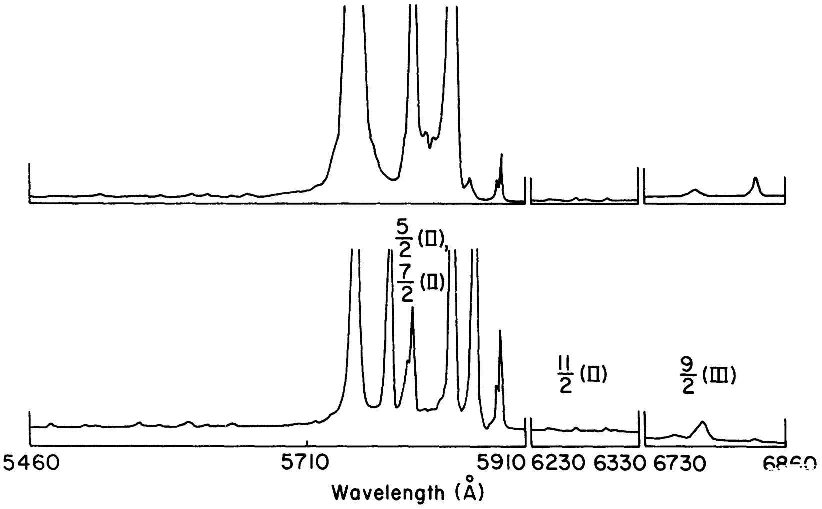

FIG. 2. Absorption spectra of $PbMoO_4 : Nd^{3+}$ taken between 5460 and 6860 Å using a conduction Dewar filled with liquid helium. The π-polarization spectrum is given on the top and the σ-polarization spectrum is presented on the bottom.

overlap among the lines within these groups makes the task of identification somewhat difficult and not completely reliable.

The Stark components of the ground-state $^4I_{9/2}$ inferred from the temperature-dependent spectra show almost perfect agreement with Kariss and Feofilov's fluorescence data.[10] For $^4I_{15/2}$ these authors reported only seven Stark levels. Shekun's calculations[11] predict the missing level at about 6175 cm^{-1}. We observed in our spectra taken on the Cary-14 spectrophotometer a weak transition to a Stark level having nearly the energy predicted by Shekun. For $\frac{11}{2}$ (I) and $\frac{13}{2}$ (I) levels the data of Shekun are used. Based on these combined results we have been able to establish the experimental center of gravity for 17 different $[SL]\,J$ levels that could be used in the calculations that follow.

V. DETAILS OF CALCULATIONS

A. Free-Ion Energy Levels

For a free-ion containing N electrons, the nonrelativistic Hamiltonian can be written

$$H = H_{cf} + H_{Coul.} + H_{so} \quad , \tag{1}$$

where H_{cf}, $H_{Coul.}$, and H_{so} are the central-field, Coulomb, and spin-orbit terms, respectively. The last two terms are treated as perturbations over the central-field Hamiltonian. A typical element of the perturbation matrix is of the form

$$E = A_1E^1 + A_2E^2 + A_3E^3 + A_4\zeta_{4f} + A_5\alpha + A_6\beta + A_7\gamma + A_8Y(22,1) + A_9Y(22,3) \quad , \tag{2}$$

where the A_i terms are the angular portions of the

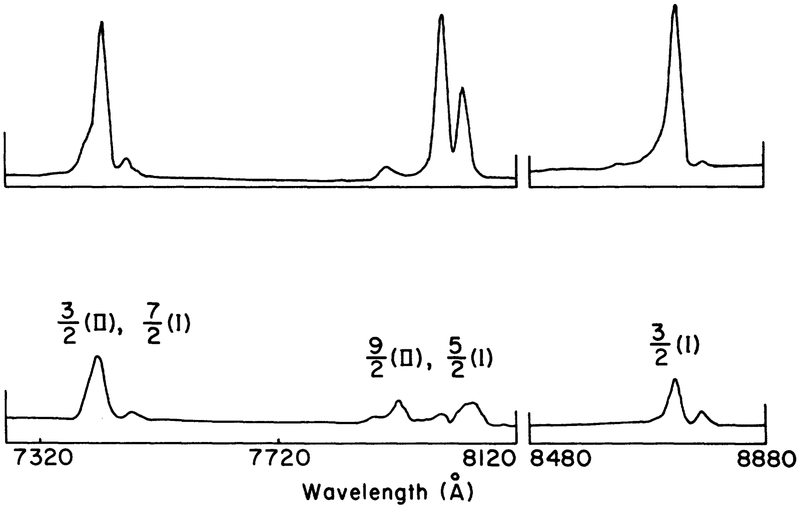

FIG. 3. Absorption spectra of $PbMoO_4 : Nd^{3+}$ taken between 7320 and 8880 Å using a conduction Dewar filled with liquid helium. The π-polarization spectrum is given on the top and the σ-polarization spectrum is presented on the bottom.

matrix elements and the remaining expressions represent the radial parts for which the usual notation has been used. In Eq. (2), the first four terms represent the isolated-configuration approximation[19]; the next three terms arise from the so-called linear-configuration interactions[19]; and the last two terms represent the dominant contributions from the nonlinear-configuration interactions.[20]

In our initial calculations, the free-ion energy matrices for Nd^{3+} were constructed in the intermediate-coupling scheme for the isolated configuration $(4f^3)$. The four radial quantities E^1, E^2, E^3 and ζ_{4f} were adjusted in a least-squares analysis of the 17 free-ion levels established from our data. The initial set of parameters for Nd^{3+} was chosen from the early work of Wybourne.[21] The final set of parameters obtained neglecting configuration interaction is $E^1 = 5017.9$, $E^2 = 25.6$, $E^3 = 485.1$, and $\zeta_{4f} = 877.9$ (all in cm^{-1}) with an rms deviation of 66 cm^{-1} as shown in Table I. However, in this calculation we note that the calculated energy positions for the $\frac{3}{2}$ (II), $\frac{7}{2}$ (II), $\frac{5}{2}$ (II), and $\frac{5}{2}$ (III) levels differ substantially from the observed levels. Furthermore, we obtained calculated values of $\frac{7}{2}$ (I) and $\frac{3}{2}$ (II) levels that are reversed from the order of increasing energy levels observed experimentally. This observation has been reported by other investigators.[6,22] To improve the agreement between our calculated and observed levels, the $\frac{7}{2}$ (I), $\frac{3}{2}$ (II), $\frac{7}{2}$ (II), and $\frac{5}{2}$ (II) levels were excluded from one of the minimization runs with the result that the rms deviation did diminish to 34 cm^{-1} for the remaining 13 levels even though the parameters essentially remained unchanged. However, to improve our calculation by being able to include all levels we felt we knew based on the experimental data, it became obvious that we must look beyond the isolated-configuration approximation to account for whatever differences that still persisted.

Before giving the results of calculations involving configuration interactions, a few relevant comments are in order. Strong crystalline fields will not only split the free-ion J levels by sizable amounts but will also shift the relative energy positions. For $LaCl_3 : Nd^{3+}$[23] such energy shifts are reported to be of the order of 20 cm^{-1}. These shifts can be expected to be even larger for $PbMoO_4 : Nd^{3+}$ because of the somewhat larger crystal-field effects. It becomes increasingly difficult to decide whether the relative energy shifts just described are primarily due to the inadequacy of the free-ion calculations or because of our neglect of J-J mixing effects. Thus, we extended our calculations to include configuration interactions not so much to improve the rms deviation but to see if some glaring individual discrepancies can be removed.

The inclusion of the parameters α, β, and γ [see Eq. (2)] in the minimization procedures did not improve the agreement in any way. We can perhaps make the cautious observation that the interactions represented by these parameters do not appear to be operative in this system. Next we included in our calculations the nonlinear parameters $Y(22, 1)$ and $Y(22, 3)$. For lanthanides $Y(22, 3)$ is negative in sign.[20] The sign of $Y(22, 1)$ depends upon the relative strengths of the interactions of $4f^3$ with $4f^2 n'p$ and $n'p^5 4f^4$ configurations. An inspection of the angular parts previously reported[20] that are associated with the $Y(kk', l')$ parameters suggests that in order to improve the agreement for the $\frac{3}{2}$ (II) level, $Y(22, 1)$ should be positive in sign. This in turn implies that the $4f^3$-$n'p^5 4f^4$ interaction is stronger than the $4f^3$-$4f^2 n'p$ interaction. In the minimization rountine involving six parameters the initial values of $Y(22, 1)$ and $Y(22, 3)$ were taken from Rajnak's work[20] on $Nd^{3+} : LaCl_3$. The resulting rms deviation is 38 cm^{-1} as can be seen from Table I. The experimentally observed order of $\frac{3}{2}$ (II) and $\frac{7}{2}$ (I) levels is now properly restored. Moreover, the agreement for the $\frac{3}{2}$ (II) and $\frac{5}{2}$ (III) levels is considerably improved and the effect on the $\frac{7}{2}$ (II) and $\frac{5}{2}$ (II) levels, though small, is nevertheless in the right direction. At this stage in our calculation, α, β, and γ were reintroduced to see if they would affect an improvement in the presence of the parameters $Y(22, 1)$ and $Y(22, 3)$. However, they failed to further improve our free-ion calculations.

B. Crystal-Field-Splitting Calculations

The crystal-field Hamiltonian of Nd^{3+} entering substitutionally at the Pb^{2+} site in $PbMoO_4$ can be written

$$H_{\text{cry}} = \sum_{k=2,4,6} B_0^k C_0^{(k)} + \sum_{k=4,6}{}' \left[B_4^k (C_4^{(k)} + C_{-4}^{(k)}) + i B_4'^k (C_4^{(k)} - C_{-4}^{(k)}) \right] , \quad (3)$$

where B_q^k and $B_q'^k$ are the real and imaginary parts of the radial quantities and where $C_q^{(k)}$ are the normalized spherical harmonics. The crystal field lifts all degeneracy except the Kramers's twofold degeneracy. The crystal-field-split levels of Nd^{3+} transform according to (Γ_5, Γ_6) or (Γ_7, Γ_8) irreducible representations of the double group S_4. The levels represented by representations within the brackets are degenerate. The basis functions for Γ_6 and Γ_7 have been listed by Sharma and Artman.[14] Basis functions for Γ_5 and Γ_8 can be obtained easily from these.[24] There are no nonzero matrix elements of H_{cry} between states belonging to different representations. It is sufficient to construct the crystal-field energy matrices for only one representation of each degenerate pair. For computational purposes the complex matrices were converted into real matrices.

Transitions from the ground state to the $\frac{7}{2}$ (II) and $\frac{5}{2}$ (II) levels include extensive vibrational and satellite structure that makes it difficult to establish with certainty the energy of the zero-phonon transitions. Moreover, since these two levels are very near to each other, energywise J-J mixing effects are expected to be large. For that reason, these levels are not included in a first-order crystal-field-splitting analysis. For reasons to be explained later, $\frac{11}{2}$ (II) and $\frac{9}{2}$ (IV) levels were also left out.

The crystal-field-splitting calculations were done first assuming D_{2d} site symmetry for which $B_4^{\prime 4}$ and $B_4^{\prime 6}$ (in cm^{-1}) are identically zero. The initial values of the remaining parameters, namely, B_0^2, B_0^4, B_0^6, B_4^4, and B_4^6 all in cm^{-1}, were taken from the work of Sengupta *et al.*[12] The results of our crystal-field-splitting calculation are included in Table I. The rms deviation for 54 Stark levels is 13.7

TABLE I. Calculated and observed crystalline Stark levels for $PbMoO_4:Nd^{3+}$.

	Center of gravity (cm^{-1})			Energy (cm^{-1}) of Stark levels relative to center of gravity		
J level	Calc. w/o C. I.[a]	Calc. with C. I.[b]	Expt.	Expt.	Γ_n	Calc.[c]
$\frac{9}{2}$ (I)	165	165	165	198.5	Γ_7	195.4
				51.5	Γ_6	36.4
				−13.5	Γ_6	−10.1
				−72.5	Γ_7	−52.8
				−164.5	Γ_7	−168.9
$\frac{11}{2}$ (I)[d]	2027	2031	2048	113.3	Γ_7	90.8
				86.3	Γ_6	78.3
				−12.7	Γ_6	1.5
				−45.7	Γ_7	−33.8
				−55.7	Γ_6	−54.7
				−85.7	Γ_7	−82.1
$\frac{13}{2}$ (I)[d]	4011	4018	4027	112.0	Γ_7	98.5
				112.0	Γ_6	98.2
				69.0	Γ_6	65.3
				−34.0	Γ_7	−16.0
				−67.0	Γ_6	−65.0
				−82.0	Γ_7	−79.2
				−109.0	Γ_6	−101.8
$\frac{15}{2}$ (I)[d]	6071	6080	6075	198.0	Γ_6	176.1
				152.0	Γ_6	142.7
				121.0	Γ_7	152.1
				100.0	Γ_7	108.2
				−65.0	Γ_7	−78.5
				−129.0	Γ_7	−131.8
				−165.0	Γ_6	−164.7
				−210.0	Γ_6	−204.1
$\frac{3}{2}$ (I)	11 491	11 116	11 422	28.0	Γ_6	32.7
				−28.0	Γ_7	−32.7
$\frac{5}{2}$ (I)	12 519	12 448	12 453	43.0	Γ_6	54.6
				−6.0	Γ_6	−17.8
				−37.0	Γ_7	−36.8
$\frac{9}{2}$ (II)	12 606	12 564	12 604	80.5	Γ_7	94.9
				48.5	Γ_6	24.7
				15.5	Γ_7	27.2
				−50.5	Γ_7	−65.9
				−94.5	Γ_7	−80.9
$\frac{7}{2}$ (I)	13 488	13 419	13 430	62.0	Γ_7	60.1
				36.0	Γ_6	50.9
				−37.0	Γ_6	51.0
				−61.0	Γ_7	−60.0
$\frac{3}{2}$ (II)	13 353	13 501	13 513	2.0	Γ_6	3.1
				−2.0	Γ_7	−3.1
$\frac{9}{2}$ (III)	14 767	14 705	14 708	81.0	Γ_7	87.9
				37.0	Γ_6	28.0
				27.0	Γ_7	26.1
				−62.0	Γ_7	−61.8
				−84.0	Γ_6	−80.3
$\frac{11}{2}$ (II)[e]	15 905	15 869	15 917	76.0	Γ_6	35.9
				66.0	Γ_7	18.7
				18.0	Γ_6	−3.9
				−24.0	Γ_7	−4.1
				−53.0	Γ_6	−20.5
				−83.0	Γ_7	−26.1
$\frac{7}{2}$ (II)[e]	17 152	17 144	17 050	57.0	Γ_7	25.8
				17.0	Γ_6	10.7
				−2.0	Γ_6	−17.9
				−71.0	Γ_7	−18.5
$\frac{5}{2}$ (II)[e]	17 205	17 225	17 297	86.0	Γ_6	132.3
				−11.0	Γ_7	−42.7
				−75.0	Γ_6	−89.6
$\frac{7}{2}$ (III)	18 999	18 909	18 956	74.0	Γ_7	71.4
				24.0	Γ_6	36.8
				−47.0	Γ_6	−20.7
				−52.0	Γ_7	−87.4
$\frac{9}{2}$ (IV)[e]	19 462	19 477	19 451	67.0	Γ_7	12.7
				44.0	Γ_8	30.8
				12.0	Γ_6	−18.8
				−42.0	Γ_7	−0.3
				−80.0	Γ_7	−24.4
$\frac{15}{2}$ (II)[f]	20 923	20 921	21 278			
$\frac{9}{2}$ (V)[f]	20 959	20 941				
$\frac{3}{2}$ (III)[f]	21 318	21 304				
$\frac{11}{2}$ (III)[f]	21 519	21 538				
$\frac{1}{2}$ (I)	23 186	23 205	23 166			
$\frac{5}{2}$ (III)	23 621	23 689	23 727	74.0	Γ_6	82.4
				−15.0	Γ_6	−10.2
				−59.0	Γ_7	−72.2

[a] The parameters used in this calculation are $E^1=5017.9$, $E^2=25.6$, $E^3=485.1$, $\zeta_{4f}=877.9$ (all in cm^{-1}); the rms deviation for 17 J levels is 66 cm^{-1}.

[b] The parameters used in this calculation are $E^1=4924.2$, $E^2=24.3$, $E^3=471.7$, $\zeta_{4f}=879.1$, $Y(22, 1)=3455.0$, $Y(22, 3)=-12019.7$ (all in cm^{-1}); the rms deviation is 38 cm^{-1}.

[c] The crystal-field-splitting calculation made use of free-ion parameters in footnote b. and the crystal-field parameters are $B_0^2=428.2$, $B_0^4=-592.2$, $B_0^6=-104.1$, $B_4^4=-914.9$, $B_4^6=-691.8$ (all in cm^{-1}); the rms deviation for 54 crystalline Stark levels is 13.7 cm^{-1}.

[d] Data reported for these J levels are taken from Refs. 10 and 11. However, these sources have not reported the polarizations for $\frac{15}{2}$ (I). The Γ_i assignments for this level are based on our experimental data.

[e] Not included in the crystal-field-splitting calculations involving a least-squares-fitting subroutine.

[f] Not included in the free-ion calculations involving a least-squares-fitting subroutine.

cm^{-1}. We see in Table I that the $\frac{9}{2}$ (II) and $\frac{7}{2}$ (III) J-level splittings show more than average disagreement. For these levels J-J mixing effects are expected to be quite large. The experimental and predicted splittings of $\frac{11}{2}$ (II) and $\frac{9}{2}$ (IV) levels show unusually large disagreement. These discrepancies persisted even when these two levels were included in the fitting calculations. It may be argued that the $\frac{9}{2}$ (IV) level being very close to $\frac{7}{2}$ (III) level should show appreciable J-J mixing effects; however, we cannot offer any explanation at the moment for the large discrepancy in the case of the rather well-isolated $\frac{11}{2}$ (II) level. It is, however, relevant to point out that similar discrepancies for this level have also been reported elsewhere.[6,22]

Only recently the results of calculations involving the actual site symmetry S_4 have been reported in the literature. In some cases, the imaginary terms $B_4'^4$ and $B_4'^6$ are known to be small,[12,25] while in other instances, fairly large values for these parameters have been reported.[14,15] However, for the calculations reported here, we find that the imaginary parameters do not improve the agreement whatsoever and, furthermore, unique values for these parameters could not be ascertained. Furthermore, we find in Sec. V C that the crystal-field-splitting wave functions, assuming D_{2d} symmetry, do indeed predict the Zeeman splittings rather well. For that reason, we have decided to ignore the imaginary terms in the following calculations.

C. Zeeman Splittings

Our primary aim in carrying out the Zeeman measurements was to test the accuracy of the crystal-field wave functions obtained in Sec. V B. These measurements were carried out with the magnetic field H parallel to the c axis of the crystal. For magnetic fields easily obtained in the laboratory (up 24 000 G in our case) the magnetic interaction $[H_M = \mu_B \vec{H} \cdot (\vec{L} + 2\vec{S})]$ is a small perturbation and the Zeeman splittings can be calculated using the crystal-field wave function as the zero-order wave functions. In the presence of the magnetic field each of the Kramers doublets will split into two levels separated by

$$\Delta E_M = \mu_B H |s_{\parallel}| \quad , \tag{4}$$

where the splitting factor $s_{\parallel}$ is defined as

$$s_{\parallel} = 2 \sum_{\gamma SL} R^2(\gamma SLJ)\, g(SLJ) \sum_{J_z} |c(J_z)|^2 J_z . \tag{5}$$

The coefficients $R(\gamma SLJ)$ and $c(J_z)$ result from the diagonalization of the free-ion and crystal-field energy matrices, respectively, and the $g(SLJ)$ values are the appropriate Lande g factors. The experimental values of ΔE_M can be obtained from the optical Zeeman measurements after making due corrections for the magnetic splitting of the ground state. For $\mathrm{PbMoO_4:Nd^{3+}}$, the ground state is a (Γ_7, Γ_8) doublet. Transitions to (Γ_5, Γ_6) levels will appear in both σ and π polarizations.[17] The observed Zeeman splitting in one polarization corresponds to the sum and the other to the difference of the magnetic splittings of the upper and ground levels. The description for transitions between (Γ_7, Γ_8) and (Γ_7, Γ_8) levels is not so simple but the results can be interpreted to a fair degree of certainty.

The calculated and measured Zeeman splittings are compared in Table II. We notice that the overall agreement is quite good. No additional parametrization was involved in this calculation and the crystal-field-splitting wave functions were determined without J-J mixing. For 25 magnetic splittings measured in σ polarization all except two (at 15 864 and 18 905 cm^{-1}) show fair agreement. There are only a few cases where the calculated and measured splittings differ by a factor of 2 or more. Similarly, in π polarization, out of the 8 Stark levels for which Zeeman measurements

TABLE II. Calculated and observed Zeeman splitting for $\mathrm{PbMoO_4:Nd^{3+}}$.

Level	Stark component (cm^{-1})	Polarization	ΔE_π (cm^{-1}) Calc.[a]	Expt.[b]	ΔE_σ (cm^{-1}) Calc.[a]	Expt.[b]
$\frac{5}{2}$ (I)	12 417	σ			2.4	2.0
	12 448	π, σ	1.0	2.5	1.8	2.4
	12 497	π, σ	0.3	3.1	3.1	3.3
$\frac{9}{2}$ (II)	12 510	π, σ	1.0	2.5	1.7	2.8
	12 554	σ			4.5	4.1
	12 620	σ			4.9	7.8
$\frac{7}{2}$ (I)	13 369	σ			1.8	1.4
	13 393	π, σ	1.6	1.9	1.2	
	13 466	π, σ	1.2		4.0	4.2
	13 493	σ			6.2	6.9
$\frac{3}{2}$ (II)	13 511	σ			3.3	3.0
	13 515	π, σ	7.2	7.2	4.4	4.3
$\frac{9}{2}$ (III)	14 624	π, σ	0.3		3.0	5.9
	14 646	σ			1.6	2.2
$\frac{11}{2}$ (II)	15 834	σ			5.3	3.9
	15 864	π, σ	6.7		3.9	1.1
	15 893	σ			4.3	3.4
	15 935	π, σ	3.6		6.4	3.7
$\frac{7}{2}$ (III)	18 905	σ			0.2	1.9
	18 909	π, σ	3.8	4.3	1.1	1.6
	18 980	π, σ	3.0	4.3	5.8	7.1
	19 030	σ			3.1	3.1
$\frac{9}{2}$ (IV)	19 409	σ			5.5	10.6
	19 463	π, σ	0.6		2.2	5.1
	19 518	σ			5.0	4.1
$\frac{1}{2}$ (I)	23 166	σ			2.0	2.1
$\frac{5}{2}$ (III)	23 712	π, σ	4.3	8.4		

[a] Based on free-ion parameters, intermediate-coupling wave functions, crystal-field parameters, and the corresponding first-order crystal-field-splitting wave functions used in Table I.

[b] Magnetic field (21 290 ± 50 G) parallel to crystallographic c axis.

could be made only one (at 12 497 cm^{-1}) shows a large discrepancy. We will not make any serious effort to explain these discrepancies but would like to emphasize the fact that the over-all agreement is quite satisfying. This observation leads us to believe that the first-order crystal-field-splitting wave functions appear reasonable. One of the peculiar features of the level at 12 497 cm^{-1}, which shows the greatest disagreement, is that $\Delta E_\pi \approx \Delta E_\sigma$: this is possible only if the ground-state splitting is zero. A somewhat similar situation exists for the levels at 12 448 and 12 510 cm^{-1}. We do not have any definite explanation for these discrepancies. However, these levels have very strong satellite structures associated with the zero-phonon transitions. Perhaps there is uncertainty on our part in observing the appropriate splitting.

We should point out that it was our inability to explain the Zeeman data for the $\frac{7}{2}$ (I) and $\frac{3}{2}$ (II) levels that made us suspect the reversal in order of increasing energy of these levels predicted earlier by our four-parameter free-ion energy-level calculation.

The values for the ground-state splitting inferred from the observed ΔE_π and ΔE_σ values for the levels at 13 515, 18 909, and 18 980 cm^{-1} are 1.4, 1.35, and 1.4 cm^{-1}, respectively, for a magnetic field of 21 290 ± 50 G parallel to the crystallographic *c* axis. Our calculated value for the ground-state splitting is 1.407 cm^{-1} under similar conditions using the first-order crystal-field-splitting wave functions generated with the crystal-field parameters reported in Table I. Our calculated value is in excellent agreement with the average value of 1.39 cm^{-1} we have deduced from our optical Zeeman data. Furthermore, our calculated and observed values are in better agreement with the value of 1.351 cm^{-1} deduced from EPR studies[26] than the calculated values of Shekun[11] (1.467 cm^{-1}) and Sengupta *et al.*[12] (1.283 cm^{-1}). Sengupta *et al.*[12] did obtain, however, better agreement in one of their calculations when they varied one of the crystal-field-splitting parameters.

VI. CONCLUSIONS

The absorption spectra of $PbMoO_4:Nd^{3+}$ has been investigated between 5500 and 25 000 cm^{-1} at 4.2, 77, and 300 °K. The structure of the ground level $\frac{9}{2}$ (I) has been established from a comparison of high- and low-temperature data. Except for the overlapping levels $\frac{15}{2}$ (II), $\frac{11}{2}$ (III), $\frac{9}{2}$ (V), $\frac{3}{2}$ (III), and the missing level $\frac{13}{2}$ (II) all *J* levels have been well identified. Unassigned transitions in the spectra fall into three categories: (i) some of them disappear on charge compensation; (ii) others can be associated with the vibronic spectrum; and (iii) the remaining transitions can be identified as belonging to the satellite structure which probably arises from crystal imperfections[16] or inequivalent site symmetries. The isolated-configuration approximation is reasonably successful in explaining the observed free-ion levels except for some individual discrepancies. The linear-configuration interaction terms seem to make little difference in the calculation but the nonlinear terms [specially those associated with $Y(22,1)$ and $Y(22,3)$] go a long way in removing the above discrepancies and greatly improving the over-all agreement. We strongly feel that any further improvement will depend on how accurately we can handle the crystal-field interactions.

The crystal-field calculations were carried out with D_{2d} as well as S_4 point-group symmetries. Our calculations failed to resolve unambiguously the question of whether D_{2d} symmetry is adequate or not; however, we tend to believe that the error introduced by considering D_{2d} and not S_4 symmetry is much less than the error introduced by neglecting *J*-*J* mixing effects. Inclusion of *J*-*J* mixing effects is a difficult task for us at the moment. Rough estimates show that if the $J=\frac{9}{2}$ and $\frac{11}{2}$ levels are allowed to mix, then even the lower levels seem to be shifted by as much as the rms deviation claimed in this work.

The crystal-field wave functions obtained from our calculations were tested for their predicted magnetic splittings. It is quite satisfying to report that by and large there is a good agreement between the calculated splittings and those obtained from Zeeman measurements.

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Green's-Function Theory of an Antiferromagnet

Dipan K. Ghosh*

H. H. Wills Physics Laboratory, Royal Fort, Tyndall Avenue, Bristol BS 8 1TL, United Kingdom

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A Green's-function theory is developed for a Heisenberg antiferromagnet using a decoupling scheme which conserves the frequency moments of the spectral function. The method closely follows Tahir-Kheli's decoupling scheme for a ferromagnetic system, and various correlation functions, sublattice magnetization, and susceptibilities are obtained. The theory is compared with the low- and high-temperature series expansions. The Néel temperature obtained using the theory is used to estimate $|J|/k_B$ values of some transition-metal compounds. The theory is then applied to one and two dimensions, and it is found to lend support to Stanley and Kaplan's suggestion of a second-order phase transition, while not predicting spontaneous magnetic ordering.

I. INTRODUCTION

The Heisenberg model of the spin-spin interaction to describe various magnetic properties of materials continues to be of interest even today. The model consists of a finite array (a linear chain in one dimension, a square in two dimensions, and a cubic structure in three dimensions) of points which may be thought of as vertices of unit spacing and side L. Periodic boundary conditions are assumed. The system of spins interact through an isotropic exchange between the nearest-neighbor sites. The Hamiltonian for such a system is given by

$$\mathcal{H} = J \sum_{i,j}{}' \vec{S}_i \cdot \vec{S}_j - \mu_B H \sum_i S_i^z \ , \tag{1.1}$$

where the prime on the summation indicates that the sum is only restricted to nearest-neighbor pairs. In spite of the inherent simplicity of the model, it remains essentially a many-body problem and an exact solution for quantities such as the partition function have not been found in any dimension. The ferromagnetic ground state and the low-lying excited states of the system were found by Bloch,[1] who also showed that the deviation from the ground-state magnetization was proportional to $T^{3/2}$. Dyson[2] in 1956 presented a theory of spin-wave interactions, which is useful in discussing the low-temperature thermodynamics of the ferromagnetic system ($J < 0$).

The development on the antiferromagnetic Heisenberg model, however, has not been so encouraging. The exact antiferromagnetic ground state of the Hamiltonian (1.1) (with $J > 0$) is not known in any dimension even though Bethe[3] and Hulthén[4] have computed the ground-state energy of the antiferromagnetic linear chain. des Cloizeaux and Pearson,[5] discussed the low-lying excitation spectrum of the antiferromagnetic chain and found that the long-wavelength magnons obey a linear dispersion law. The statistical theories of the model historically date back to the molecular-field theory of Néel,[6] which successfully explained the existence of a transtion temperature, a specific-heat anomaly, etc., but failed to explain the lack of short-range order above the transition temperature and many other low-temperature properties. Series expansions by Opechowski[7] at high temperatures and spin-wave theories at low temperatures have their validities in restricted range of temperatures but are unreliable near the transition