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Interpretation of the optical absorption spectrum and of the paramagnetic susceptibility of NdAlO₃

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The absorption spectrum of pure rhombohedral $NdAlO_3$ was determined at 4.2 K from 10 000 to 34 000 cm^{-1}. Adding the levels determined for the ^4I multiplet by other authors, a total of 117 Stark levels was obtained. They were fitted to a mean square deviation of 13 cm^{-1} with a Hamiltonian involving 12 free atom parameters and six D_3 crystal field parameters applied on the 364 kets basis in the $4f^3$ configuration. The values are $B_0^2 = -481$ cm^{-1}, $B_0^4 = 481$ cm^{-1}, $B_3^4 = -390$ cm^{-1}, $B_0^6 = -1700$ cm^{-1}, $B_3^6 = -950$ cm^{-1}, $B_6^6 = -1080$ cm^{-1}. Free atom parameters are very close to those of Nd^{3+} in LaCl$_3$. The powder paramagnetic susceptibility was measured from 4 to 1000 K. The $1/\chi$ versus T curve shows a pronounced curvature, even below 300 K, which is fairly well reproduced by a crystal-field-only calculation involving the complete wave vectors of the 18 lowest Kramers doublets.

I. INTRODUCTION

A complete analysis of the energy level sequence of Nd^{3+}, $4f^3$, up to 30 000–40 000 cm^{-1} has been reported only for a limited number of compounds that is Nd^{3+} in LaCl$_3$,[1] Nd^{3+} in LaF$_3$,[2,3] Nd (NO$_3$)$_3$ · 6H$_2$O,[4] and Nd$_2$O$_3$.[5] The present work reports the experimental determination of the absorption spectrum at 4 K of NdAlO$_3$ between 10 000 and 34 000 cm^{-1}, and the interpretation of the data taking into account the Stark levels of the ground ^4I multiplet as established by Finkman, Cohen, and van Uitert.[6] In all 117 levels were fitted. The same Hamiltonian used previously[4,5] was applied on the basis of the 364 $|SLJM_J\rangle$ kets in the configuration. It involves 12 free-atom parameters (three Racah parameters, the spin–orbit coupling constant, two of the three Trees parameters, the six three-body Judd parameters) and the six crystal field parameters of the D_3 crystal field Hamiltonian written in Wybourne's formalism.[7]

The wave vectors and the energies obtained for the 18 lowest Kramers doublets were used to compute the paramagnetic susceptibility parallel, perpendicular and mean from 4 to 1000 K. The mean (powder) paramagnetic susceptibility was thereafter experimentally measured and compared to the calculation.

II. CRYSTALLOGRAPHIC BACKGROUND

NdAlO$_3$ like LaAlO$_3$ and PrAlO$_3$ is a rhombohedric structure derived from the perovskite one which belongs to the space group $R\bar{3}C$.[8,9] The coordination polyhedron around the rare earth at the D_3 site symmetry (a case of coordination 12) is described for LaAlO$_3$ in Ref. 10. It is quite easy to grow single crystals of NdAlO$_3$ from flux[11]; however, there is a critical problem in the crystals which is the very high degree of twinning. Marezio *et al.*[9] had to use a highly twinned crystal to refine the structure. Twinning is due to the fact that as a consequence of the transition from cubic to rhombohedral, any one of the four threefold axes in the cubic perovskite structure can become the trigonal axis. Each orientation of the axis will yield a domain. "In NdAlO$_3$ the domains are finite in one direction and extend to the limit of the crystal in the other two directions. If one applies light pressure on one of these polydomain crystals in a general crystallographic direction the number of domains increases".[9] Because of the severity of this twinning problem one cannot do with too much confidence experiments on the crystals with respect to the ternary axis of the trigonal structure this because the axis direction may be continuously changing within the sample in an unknown way. Due to this extended twinning optical polarization experiments or paramagnetic susceptibility measurements with respect to the crystal axis are not usually easily feasible.

III. EXPERIMENTAL DATA

NdAlO$_3$ was prepared as a powder by melting an equimolar mixture of Nd$_2$O$_3$ and Al$_2$O$_3$ at the focus of a 2 kW Solar Furnace at the CNRS facilities in Odeillo, France. The sample was checked through a Guinier x-ray camera. The spectrum was taken with the sample in between two quartz plates immersed in liquid helium. It was illuminated by the white light from a Xenon 150 W Osram HBO lamp and the absorptions were recorded on a photographic plate through a 3.4 m Jarrell-Ash spectrograph with a 590 line/mm grating. A 1 m Jarrell-Ash 78460 Czerny–Turner was also used. The reference wavelengths were from the iron arc and corrected for vacuum. The experimental data are collected in Table I.

IV. CRYSTAL FIELD PARAMETERS

A set of free-atom parameters suitable as a starting point for fitting the experimentally recorded levels is obtained from the work of Finkman *et al.*[6] who determined it from 26 Stark levels of the ^4I multiplet of Nd^{3+} in NdAlO$_3$. The crystal field parameters for Eu^{3+} in LaAlO$_3$ are also known from a study of 17 Stark levels of the ^7F multiplet.[10]

The D_3 crystal field Hamiltonian involves six B_q^k crystal field parameters and is consequently analogous to a C_{3v} Hamiltonian. The differences in the tensor operators for the two symmetries are only in the odd components which are not to be taken into account in the Hamiltonian because of the rule that k should be even.

TABLE I. Energy levels of Nd^{3+} in $NdAlO_3$.

TABLE I (*Continued*)

Nominal state	Symmetry	E_{calc} (cm^{-1})	E_{exptl} (cm^{-1})	$E_{exptl} - E_{calc}$ (cm^{-1})	Remarks
$^4I_{9/2}$	$D_{1/2}$	0	0	0	
$^4I_{9/2}$	$D_{1/2}$	122	122	0	
$^4I_{9/2}$	S_1+S_3	154	148	-6	
$^4I_{9/2}$	$D_{1/2}$	584	599	15	
$^4I_{9/2}$	S_1+S_3	584	599	15	
$^4I_{11/2}$	$D_{1/2}$	2046	2056	10	
$^4I_{11/2}$	S_1+S_3	2070	2078	8	
$^4I_{11/2}$	$D_{1/2}$	2206	2212	6	a
$^4I_{11/2}$	S_1+S_3	2274	2278	4	
$^4I_{11/2}$	$D_{1/2}$	2290	2295	5	
$^4I_{11/2}$	$D_{1/2}$	2308	2321	13	
$^4I_{13/2}$	$D_{1/2}$	3961	3968	7	
$^4I_{13/2}$	S_1+S_3	4074	4080	6	
$^4I_{13/2}$	$D_{1/2}$	4117	4117	0	
$^4I_{13/2}$	$D_{1/2}$	4162	4159	-3	a
$^4I_{13/2}$	$D_{1/2}$	4269	4274	5	
$^4I_{13/2}$	S_1+S_3	4276	4278	2	
$^4I_{13/2}$	$D_{1/2}$	4440	4442	2	
$^4I_{15/2}$	$D_{1/2}$	5747	5738	-9	
$^4I_{15/2}$	S_1+S_3	6005	5977	-28	
$^4I_{15/2}$	$D_{1/2}$	6028	6021	-7	a
$^4I_{15/2}$	$D_{1/2}$	6276	6273	-3	
$^4I_{15/2}$	$D_{1/2}$	6321	6309	-12	
$^4I_{15/2}$	S_1+S_3	6359	6336	-23	
$^4I_{15/2}$	$D_{1/2}$	6743	6737	-6	
$^4I_{15/2}$	S_1+S_3	6760	6761	1	
$^4F_{3/2}$	S_1+S_3	11508	11517	9	
$^4F_{3/2}$	$D_{1/2}$	11584	11606	22	
$^4F_{5/2}$	$D_{1/2}$	12530	12507	-23	
$^4F_{5/2}$	S_1+S_3	12535	12507	-28	
$^2H2_{9/2}$	$D_{1/2}$	12579	12577	-2	
$^2H2_{9/2}$	S_1+S_3	12603	12602	-1	
$^4F_{5/2}$	$D_{1/2}$	12626	12636	10	
$^2H2_{9/2}$	S_1+S_3	12819	12780	-39	Large
$^2H2_{9/2}$	$D_{1/2}$	12850	12859	9	Weak
$^2H2_{9/2}$	$D_{1/2}$	12952	12947	-5	
$^4F_{7/2}$	$D_{1/2}$	13419	13413	-6	
$^4F_{7/2}$	$D_{1/2}$	13529	13522	-7	
$^4F_{7/2}$	$D_{1/2}$	13662	13666	4	
$^4S_{3/2}$	S_1+S_3	13666	13666	0	
$^4S_{3/2}$	$D_{1/2}$	13676	13666	-10	
$^4F_{7/2}$	S_1+S_3	13720	13714	-6	
$^4F_{9/2}$	S_1+S_3	14773	14772	-1	
$^4F_{9/2}$	$D_{1/2}$	14837	14836	-1	
$^4F_{9/2}$	$D_{1/2}$	14871	14878	7	
$^4F_{9/2}$	S_1+S_3	14879	14884	5	
$^4F_{9/2}$	$D_{1/2}$	14880	14884	4	
$^2H2_{11/2}$	S_1+S_3	15945	15940	-5	
$^2H2_{11/2}$	$D_{1/2}$	15949	15977	28	
$^2H2_{11/2}$	$D_{1/2}$	15965	15984	19	
$^2H2_{11/2}$	$D_{1/2}$	16014	16038	24	
$^2H2_{11/2}$	S_1+S_3	16031	16043	12	
$^2H2_{11/2}$	$D_{1/2}$	16101	16129	28	
$^4G_{5/2}$	S_1+S_3	17105	17086	-19	
$^4G_{5/2}$	$D_{1/2}$	17114	17107	-7	
$^4G_{5/2}$	$D_{1/2}$	17258	17258	0	
$^2G_{7/2}$	$D_{1/2}$	17424	17426	2	
$^2G_{7/2}$	S_1+S_3	17427	17426	-1	
$^2G_{7/2}$	$D_{1/2}$	17465	17444	-21	
$^2G_{7/2}$	$D_{1/2}$	17486	17483	-3	
$^4G_{7/2}$	$D_{1/2}$	18962	18987	25	
$^4G_{7/2}$	S_1+S_3	19006	19014	8	
$^4G_{7/2}$	$D_{1/2}$	19122	19129	7	
$^4G_{7/2}$	$D_{1/2}$	19200	19192	-8	
$^3K_{13/2}$	$D_{1/2}$	19442			
$^2K_{13/2}$	S_1+S_3	19475	19482	7	
$^4G_{9/2}$	$D_{1/2}$	19484	19482	-2	
$^4G_{9/2}$	S_1+S_3	19541			
$^4G_{9/2}$	$D_{1/2}$	19563	19562	-1	
$^2K_{13/2}$	$D_{1/2}$	19594	19598	4	Large
$^4G_{9/2}$	S_1+S_3	19605			
$^4G_{9/2}$	$D_{1/2}$	19605			
$^2K_{13/2}$	$D_{1/2}$	19723	19713	-10	
$^2K_{13/2}$	$D_{1/2}$	19760	19740	-20	Large
$^2K_{13/2}$	S_1+S_3	19836			
$^2K_{13/2}$	$D_{1/2}$	19872			
$^2G1_{9/2}$	S_1+S_3	20979	20990	11	
$^2D1_{3/2}$	$D_{1/2}$	21009	21017	8	
$^2G1_{9/2}$	S_1+S_3	21038	21030	-8	
$^2G1_{9/2}$	$D_{1/2}$	21066	21063	-3	
$^2G1_{9/2}$	$D_{1/2}$	21114	21118	4	
$^2D1_{3/2}$	S_1+S_3	21203	21200	-3	
$^2G1_{9/2}$	$D_{1/2}$	21217	21229	12	
$^4G_{11/2}$	S_1+S_3	21461	21435	-26	
$^4G_{11/2}$	$D_{1/2}$	21471			
$^2K_{15/2}$	$D_{1/2}$	21501			
$^2K_{15/2}$	S_1+S_3	21532	21518	14	
$^2K_{15/2}$	$D_{1/2}$	21563	21563	0	
$^4G_{11/2}$	$D_{1/2}$	21605	21600	-5	
$^4G_{11/2}$	$D_{1/2}$	21630			
$^2K_{15/2}$	S_1+S_3	21687	21695	8	Large
$^4G_{11/2}$	$D_{1/2}$	21741			
$^4G_{11/2}$	S_1+S_3	21763			
$^3K_{15/2}$	$D_{1/2}$	21780			
$^2K_{15/2}$	$D_{1/2}$	21830			
$^2K_{15/2}$	$D_{1/2}$	21885	21881	-4	Very large
$^2K_{15/2}$	S_1+S_3	21909			
$^2P_{1/2}$	$D_{1/2}$	23292	23284	-8	
$^2D1_{5/2}$	$D_{1/2}$	23787	23791	4	
$^2D1_{5/2}$	S_1+S_3	23888	23882	-6	
$^2D1_{5/2}$	$D_{1/2}$	23944	23946	2	
$^2P_{3/2}$	S_1+S_3	26136	26139	3	
$^2P_{3/2}$	$D_{1/2}$	26214	26214	0	
$^4D_{3/2}$	$D_{1/2}$	27933	27930	-3	
$^4D_{3/2}$	S_1+S_3	27955	27965	10	
$^4D_{5/2}$	$D_{1/2}$	28060	28059	-1	
$^4D_{5/2}$	$D_{1/2}$	28201	28194	-7	Large, strong
$^4D_{5/2}$	S_1+S_3	28211			
$^4D_{1/2}$	$D_{1/2}$	28563	28558	-5	Very large, s.
$^4I_{11/2}$	$D_{1/2}$	29131	29138	7	
$^4I_{11/2}$	S_1+S_3	29169	29176	7	
$^4I_{11/2}$	$D_{1/2}$	29183	29184	1	
$^4I_{11/2}$	$D_{1/2}$	29280	29298	18	
$^4I_{11/2}$	S_1+S_3	29283	29298	15	
$^4I_{11/2}$	$D_{1/2}$	29466			
$^2L_{15/2}$	$D_{1/2}$	29809			
$^2L_{15/2}$	S_1+S_3	29854			
$^2L_{15/2}$	$D_{1/2}$	29888	29894 } 29929 }	6	Large, strong / Not assigned
$^2L_{15/2}$	S_1+S_3	30046	30045	-1	very weak
$^4D_{7/2}$	$D_{1/2}$	30086			
$^2L_{15/2}$	$D_{1/2}$	30091			
$^4D_{7/2}$	S_1+S_3	30111			
$^4D_{7/2}$	$D_{1/2}$	30196	30195	-1	
			30211		Not assigned
$^2L_{15/2}$	$D_{1/2}$	30247	30241	-6	
$^2L_{15/2}$	S_1+S_3	30286	30274	-12	
$^4D_{7/2}$	$D_{1/2}$	30350			
			30391		Not assigned, very weak
$^2L_{15/2}$	$D_{1/2}$	30446			
$^2I_{13/2}$	$D_{1/2}$	30550			
$^2I_{13/2}$	$D_{1/2}$	30598	30575	-23	
$^2I_{13/2}$	S_1+S_3	30616	30619	3	
$^2I_{13/2}$	$D_{1/2}$	30692	30715	23	
$^2I_{13/2}$	S_1+S_3	30722	30736	14	
$^2I_{13/2}$	$D_{1/2}$	30774	30777	3	
$^2I_{13/2}$	$D_{1/2}$	30876	30901	25	Very weak
$^2L_{17/2}$	$D_{1/2}$	31353			
$^2L_{17/2}$	S_1+S_3	31376			
$^2L_{17/2}$	$D_{1/2}$	31395			
$^2L_{17/2}$	S_1+S_3	31563			
$^2L_{17/2}$	$D_{1/2}$	31575			
$^2L_{17/2}$	$D_{1/2}$	31600			
$^2L_{17/2}$	$D_{1/2}$	31777			
$^2L_{17/2}$	$D_{1/2}$	31808			
$^2L_{17/2}$	S_1+S_3	31899			
$^2H1_{9/2}$	$D_{1/2}$	32661	32658	-3	
$^2H1_{9/2}$	S_1+S_3	32687	32681	-6	
$^2H1_{9/2}$	$D_{1/2}$	32867	32870	3	
$^2H1_{9/2}$	$D_{1/2}$	32912	32911	-1	
$^2H1_{9/2}$	S_1+S_3	32947	32961	14	
$^2D2_{3/2}$	$D_{1/2}$	33262	33267	-5	
$^2D2_{3/2}$	S_1+S_3	33320			
$^2H1_{11/2}$	$D_{1/2}$	33803			
$^2H1_{11/2}$	$D_{1/2}$	34087			

a Data from Ref. 6.

TABLE II. Crystal field parameters for rare earths in $LnAlO_3$.

	B_0^2	B_0^4	B_3^4	B_0^6	B_3^6	B_6^6	Ref.
$NdAlO_3$ (4 K)	-530.4	490.3	-449.3	-1646.9	-992	-1026.6	Finkman et al.[6] set B including J mixing
Eu^{3+}: $LaAlO_3$ (77 K)	-207	440	-386	-1657	-877	-1155	Faucher and Caro[10]
$NdAlO_3$ (4 K)	-793.6	1021.4	-678.8	-1691.3	-916.3	-963.3	Finkman et al.[6] set A without J mixing

The known parameter sets are given in Table II.

It can be seen that the first two sets are very much alike, a fact which confirms that the crystal field parameters are similar for rare earths in the same structure.

V. EXCITED STATES

The splitting of the $^4I_{9/2}$ level was determined from the absorption spectrum at 300 K of the transition $^4I_{9/2} - ^2P_{1/2}$. The result was practically identical to the fluorescence determination of Finkman et al.[6] We used their experimental levels for the other components of the ^4I multiplet.

It was quite easy to assign the component of the $^{2S+1}L_J$ levels in the spectrum to the calculated values using the above crystal field parameters and free atom parameters for the chloride.[4] The fitting yielded the parameter values in Table III. One hundred seventeen levels were fitted to a mean quadratic deviation of 13 cm^{-1}. The computed levels are listed in Table I.

The crystal field parameters are very close to those given above which, according to Finkman et al.,[6] fit the ^4I multiplet alone when J mixing is taken into account. It can be seen from Table I that the set fit well the highly excited states (see for instance the $^2H(1)_{9/2}$ state at 32000 cm^{-1}). We can see here again that as far as the energies alone are concerned basically the same set of crystal field parameters can be used for the excited levels and for the ground state provided of course that

a complete $4f^3$ basis is considered because of the importance of the J-mixing phenomenon.

There is one big exception to the generally satisfactory fitting of the excited levels. It is the well known case of the $^2H(2)_{11/2}$ level around 16000 cm^{-1}. The startling discrepancy between the computed and experimental Stark splittings can be seen in Table I. An identical problem with that level has been reported for several other compounds. The misfit is extremely large for instance in $A-Nd_2O_3$.[5] The intensity of the transition from the ground state to the $^2H(2)_{11/2}$ is rather weak. However, it can be seen in Fig. 1 that the six compo-

TABLE III. Free atom and crystal field parameters for Nd^{3+} in $NdAlO_3$ at 4.2 K (corresponding to calculation in Table I).

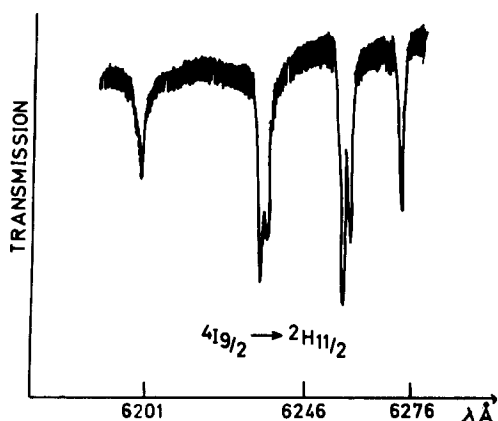| Parameter	Value (cm^{-1})	
E^0	13103	±6
E^1	4927	±2
E^2	23.23	±0.03
E^3	481	±0.9
ζ	874	±0.7
α	20.33	±0.15
β	-614	±8
γ	[750]	
T^2	247	±28
T^3	37	±3
T^4	102	±4
T^6	-270	±6
T^7	299	±13
T^8	284	±23
B_0^2	-481	±17
B_0^4	481	±37
B_3^4	-390	±26
B_0^6	-1700	±37
B_3^6	-950	±31
B_6^6	-1080	±29
Number of Stark levels	117	
Mean quadratic deviation (cm^{-1})	13	

FIG. 1. Absorption spectrum at 4.2 K for the transition from the ground state of $^4I_{9/2}$ to the six Stark levels of $^2H_{11/2}$.

nents of the $^4I_{9/2} \rightarrow {}^2H(2)_{11/2}$ transition at 4. 2 K are very
sharp in NdAlO₃ and that leaves out any explanation
through experimental incertitude to take care of the mis-
fit. As we have said before,[5] this fact remains a puzzle
in the application of crystal field theory to the $4f^3$ con-
figuration.

VI. MAGNETIC SUSCEPTIBILITY

From the knowledge of the wave vectors of the lowest
Kramers doublets it is possible to compute the diagonal
and non diagonal matrix elements of the magnetic $\mathbf{L} + 2\mathbf{S}$
operator which enters the Van Vleck formula for the
paramagnetic susceptibility.[5] The levels are more or
less populated depending on the temperature and their
energy. The Van Vleck formula uses a Boltzmann dis-
tribution.

The parallel, perpendicular, and mean paramagnetic
susceptibilities can be computed taking into account the
18 lowest Kramers doublets (that is $^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$)
a set which is sufficient to cover the thermal population
effect well above 1000 K. The $\mathbf{L} + 2\mathbf{S}$ operator matrix
elements were automatically computed with the complete
wave vectors down to the tiny components.

The $D_{1/2}$ ground state wave vector is quite well sepa-
rated from the other $^4I_{9/2}$ components. It contains
95.09% of $^4I_{9/2}$ kets, 1.67% of $^4I_{11/2}$ kets, 0.33% of
$^4I_{13/2}$ kets, 0.29% of $^2H(1)_{9/2}$ kets, 2.48% of $^2H(2)_{9/2}$
kets, a score of other components making together
0.14%. The wave vectors for the ground state or other
excited states can be obtained from the authors on re-
quest.

The measured powder susceptibility from 4 to 1000 K[12]
of our sample is reproduced Fig. 2, together with the
results of the above calculation. It is seen that it is
predicted that $1/\chi_\parallel$ is larger than $1/\chi_\perp$ and that the ex-
perimental points follow generally well the curve derived

FIG. 2. Computed paramagnetic susceptibilities parallel, per-
pendicular and mean (powder) (0–1000 K) from the wave vec-
tors of the 18 lowest Kramers doublets of the $4f^3$ configuration
with the parameters in Table III. Triangles are experimental
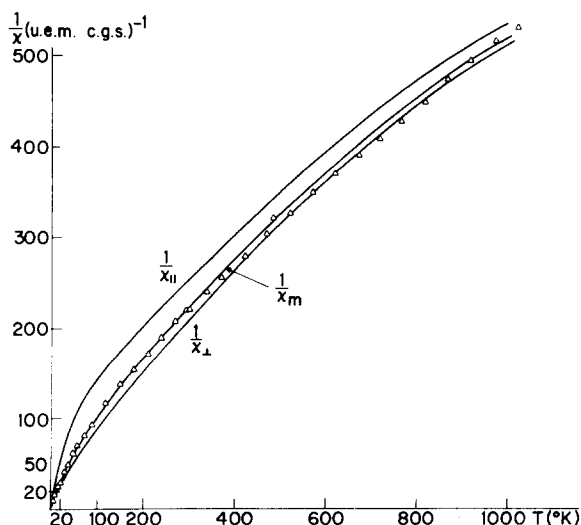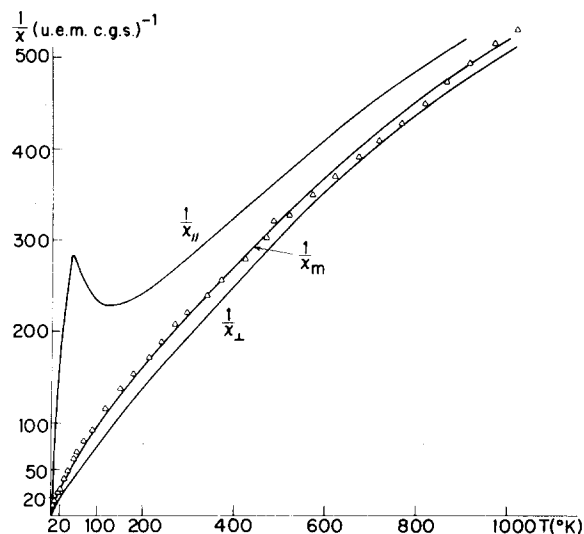measurements of Chaminade and Pouchard[12] on NdAlO₃ powder.

FIG. 3. Computed paramagnetic susceptibilities parallel, per-
pendicular and mean (powder) (0–1000 K) from the wave vectors
of the 18 lowest Kramers doublets of the $4f^3$ configuration with
the crystal field parameters set A of Finkman *et al*.[6], cf. Table
II. Triangles are powder experimental measurements.

from the interpretation of the optical data.

Among the possible alternative crystal field parame-
ter sets we tested the set A proposed by Finkman *et al*.[6]
(Table II) which gives irreducible representations and
energies (0, 127, 148, 566, 588) *for the ground state*
roughly in agreement with the experiment. Within the
complete calculation scheme the result for $1/\chi_m$ is
slightly less good. However, a curious and pronounced
maximum appeared at low temperature (25 K) on the
computed $1/\chi_\parallel$ curve for this set (Fig. 3). The reason
for this maximum is to be found in the *composition* of
the wave vectors. The ground state level with Finkman
et al.'s set A (6) is almost purely $|^4I_{9/2,1/2}\rangle$ with a coef-
ficient of 0.9075 (82%), and it is well separated (127
cm⁻¹) from the first excited level which is predominantly
$|^4I_{9/2,7/2}\rangle$ (79%). The $L_z + 2S_z$ operator diagonal matrix
element which enter the computation of $1/\chi_\parallel$ is propor-
tional to the M_J values and hence much smaller for the
ground state level than for the first excited state, and
as this one is easily depopulated because of the large dif-
ference in energy, the $\chi_\parallel$ value is decreased and $1/\chi_\parallel$ of-
fers a maximum before falling off to zero because $T \rightarrow 0$.
We checked this phenomenon for D_{3h} symmetry in which
the $M_J = 1/2$ kets are clustered within a single level be-
cause they belong to a separate irreducible representa-
tion ($_2S_2$). This level can be ground state for crystal
field parameters values such as $B_0^4 > +1000$ cm⁻¹ and
$B_0^4/B_0^6 > -1$. Those approximate conditions are in fact ·
met by the Finkman *et al*.'s A set.[6] Such values of crys-
tal field parameters seem to be rarely observed in prac-
tice. Our set for NdAlO₃ (Table III) does not give rise
to the same type of curve because the ground state level
is basically a mixture of $|^4I_{9/2,1/2}\rangle$ (44.78%) and $|^4I_{9/2,7/2}\rangle$
(36.81%) kets as B_0^4 is much smaller.

The mean susceptibility (powder) measured (Figs. 2
and 3) does not follow really a Curie–Weiss law. There
is a linear portion between 80 and 250 K with a paramag-

netic Curie temperature of -70 K and another one between 300 and 600 K with a paramagnetic Curie temperature of -160 K. The large values of these temperatures have been considered as "evidence of antiferromagnetic ordering".[13] The relative agreement between the experimental and crystal-field-only magnetic susceptibility curves (Figs. 2 and 3) shows that the curvature is entirely due to the nature of the wave functions associated with the Stark levels and *not* to an interaction between the paramagnetic neodymium atoms. It is well known[14,15] that one should be cautious in relating the negative paramagnetic Curie temperatures to antiferromagnetic interactions. In the present case it is obviously a crystal field effect.

VII. g VALUES

From the wave vectors it is easy to compute for each Kramers doublet the g values associated with it. Finkman *et al.*[6] measured $g_{||}$ for the three lower levels of the ground state. They found 1.06, 2.10, and 2.10, respectively. Our complete calculation (all kets) gives 1.81, 2.65, and 2.82, respectively. Finkman *et al.*[6] set A under the complete calculation yields 0.95, 3.57, and 2.89, respectively. The agreement is bad as the ratio between our calculated and the reported experimental values is roughly 1.5.

This type of discrepancy has been reported and discussed for lanthanides g values,[16–18] for instance for cerium in various rare earth ethylsulfates[17] where it is found that the experimental $g_{||}$ value for the $^2F_{5/2}$ Kramers doublet ground state is lower than the theoretical one by 8%–10%. Bartel and Spedding[19] computed and measured the $g_{||}$ values for several degenerate levels in thulium $(4f^{12})$ ethylsulfate. The differences are of the same order of magnitude that is in the 10% range at the maximum but either positive or negative. Birgeneau[17] suggests that they are due to electron–phonon interaction. This effect amounts to a modification of the composition of the wave vectors following the change, and the creation of new, crystal field operators as the symmetry is reduced in the course of the dynamic movement due to the vibrations. One may say that the crystal field parameters are then slightly different for each Stark level depending on the particular phonon coupling.

We have here, however, a discrepancy for larger than 10%. From the variations we explored around the values of crystal field parameters of rank $k = 4$ and 6 of the two sets which are in agreement with $^4I_{9/2}$ experimental energy levels it is clear that the $g_{||}$ values for the first and second excited states will approach their reported experimental value (2.10) only through a *drastic* change in these crystal field parameters because the computed $g_{||}$ values remain remarkably close to 3 or above despite the fact that the energies change quite fast. On the other hand, for the ground state itself, the experimental $g_{||}$ value is close to the one for Finkman *et al.* set's A^6 and appears to be very sensitive to the exact value for B_0^2.

One can argue that the g values measured by Finkman *et al.*[6] may not be absolutely right if their crystals exhibited some twinning. They suspected the problem because they experienced difficulties in interpreting the

polarization of their Raman lines, but after an examination of their crystals between cross polarizers they concluded they were not twinned. However, one may still question the observation because of the sensitivity of the structure (the crystals we have are all twinned)[9] and the possibility of microtwinning on a very small scale.

The $g_\perp$ values computed for the ground state and the first excited state of $^4I_{9/2}$ under our set of crystal field parameters are 2.83 and 1.90, respectively.

VIII. DISCUSSION

A. Free-atom parameters

The Slater–Condon integrals derived from the values in Table II are (in cm⁻¹).

$$F_2 = 322.5 \pm 1.0, \quad F_4 = 49.77 \pm 0.10, \quad F_6 = 5.13 \pm 0.02$$

values which are very close to the one we have found for Nd³⁺ in anhydrous LaCl₃ with the same type of analysis[2] that is respectively 323.8, 50.17, 5.21. The present values are slightly lower. Those values are computed at the fixed value $\gamma = 750$ cm⁻¹.[20] It is now well established[2] that the appropriate γ value is close to 1400 cm⁻¹, but the value chosen does not affect the analysis as long as the $^2F(1)$ levels in the ultraviolet are not properly identified. We keep the 750 cm⁻¹ value to permit the comparison with our previous work, E_1 and γ are strongly correlated. To convert the E_1 value for other γ values one should keep in mind that $3 E_1 + 3/5 \gamma = $ const if the ^2F levels are not among the fitted data.

The spin–orbit coupling constant is also close but slightly lower than the one found for Nd³⁺ in LaCl₃. NdAlO₃ sits on the blue side of the nephelauxetic series drawn from the $^2P_{1/2}$ position.[21] The Slater–Condon parameters derived from the present work are in agreement with this empirical observation. The present case of coordination 12 is characterized by almost unchanged free atom parameters with respect to neodymium in the anhydrous chloride (coordination nine) and larger crystal–field parameters especially of order 6 in agreement with electrostatic calculations.[10] This brings a larger ground state splitting and consequently a shifting of the spectrum to the blue when compared to the anhydrous chloride. This is markedly different from the result[5] of the analysis of the spectrum of the layered compound $(NdO)_2O$, $(A-Nd_2O_3)$, where the neodymium coordination is seven and for which the nephelauxetic effect is pronounced.

B. Crystal-field parameters

Our fit is not perfect as the 10 effective operators for additional magnetic interactions[1,20] are not used in the present study. Our overall set of crystal-field parameters is very much in agreement with the one Finkman *et al.*[6] derived from an analysis of the Stark levels in the ^4I multiplet alone. The accurate measurement of the low temperature variation of the paramagnetic susceptibility seems to be an appropriate method to check the crystal-field parameters derived from the analysis of the optical data for pure neodymium compound.

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