Energy States of Solids with Particular Reference to the Energy States of Nd2(SO4)3–8H2O

F. H. Spedding, H. F. Hamlin, and G. C. Nutting

by a comparison of Fig. 2 with Mulliken's Figs. 35–38. The unobserved levels which should be stable according to both methods of prediction are the $^3\Pi$ of BH and the $^4\Sigma^-$ of CH. It is very likely that these levels would be observed as stable states if intersystem combinations were not necessary thereto. It is very interesting that this theory confirms Mulliken's predictions for these cases, because the two approaches are basically very different.

(4) For levels involving a large amount of promotion, the predictions made here are much lower than Mulliken's and are probably quite inaccurate. The most striking examples of this are those levels which are quite stable according to this theory but are repulsive by Mulliken's prediction: $^5\Sigma^-$ of NH, $^4\Sigma^-$ and $^4\Pi$ of OH, $^3\Pi$ and $^3\Sigma^-$ of FH. Although these levels, being of higher multiplicity than the observed levels of these molecules, would in any case be difficult to observe, the concept of promotion which is the

basis of Mulliken's predictions is too well founded for one to attach much significance to the predictions here. Furthermore, there is considerable evidence that the $^3\Pi$ state of HI is repulsive—further reason for believing that state to be likewise in HF.

Thus it appears that, however lacking in rigor the simplified HLSP theory may be, it does give reasonably accurate predictions of certain levels of the molecules studied here—of the levels, that is, which involve no electron promotion. It is by no means clear why this theory should be even so accurate as it is.[21]

In conclusion, I wish to express my deep gratitude to Professor Van Vleck, whose suggestions were essential to this work, and to thank Professor Mulliken for helpful discussions.

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[21] The discussion of Coolidge and James, reference 4, throws much light on the subject, but they admit failure to explain completely the success of "semi-empirical" processes such as the one used here.

Energy States of Solids with Particular Reference to the Energy States of Nd₂(SO₄)₃·8H₂O

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(Received December 11, 1936)

The absorption spectrum of $Nd_2(SO_4)_3 \cdot 8H_2O$ crystals has been photographed at 20°, 78°, 169° and 298°K. The absorption lines occur in multiplets and originate in transitions from two low excited states as well as from the normal state. The excited levels of the basic multiplet are situated 77 and 260 cm⁻¹ above the lowest state and undoubtedly arise through splitting of the normal state of the free Nd^{+++} ion in the electric field set up by its immediate neighbors in the crystal lattice. The positions of the observed levels are not in accord with conclusions of Penney and Schlapp from their study of the influence of crystal fields on the temperature variation of the paramagnetic susceptibility of Nd ion in neodymium sulfate octahydrate. Based in part upon the susceptibility measurements of Gorter and de Haas, Penney and Schlapp's work requires that the levels be at 0, 243 and 834 cm⁻¹. If the data of Gorter and de Haas may be considered in error as regards absolute values the positions of the levels we have found are in excellent agreement with predictions of the theories of Van Vleck and Penney and Schlapp, and with the experimental results of Meyer and of Zernicke and James.

V AN VLECK[2] and his associates, using the methods of group theory and wave mechanics, have developed a very attractive theory of the behavior of such energy levels of the

common paramagnetic ions as normally contribute to their paramagnetic properties, when the ions are brought into the electric field of their neighboring atoms in a solid. Penney and Schlapp[3] have applied the theory to the specific case of $Nd_2(SO_4)_3 \cdot 8H_2O$. Making the assump-

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[2] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Oxford, 1932).

[3] W. G. Penney and R. Schlapp, Phys. Rev. **41**, 194 (1932).

TABLE I. *Frequencies of absorption lines of solid Nd₂(SO₄)₃·8H₂O.*

Left half

Ångstroms (20°K)	Wave Number (20°K)	Int.	W.N. (78°K)	Int.	W.N. (169°K)	Int.	W.N. (298°K)	Int.	Type
6838.4	14,619.	3d	14,622.	6wd					h
			14,658.	3wd					h
6801.9	14,697.	6d	14,700.	6d	14,702.	3d			l
6784.9	14,735.	6d	14,737.	6d	14,741.	4wd			l
6765.8	14,776.	6d	14,778.	6d	14,780.	4wd			
6747.7	14,816.	5d	14,817.	6d	14,820.	4wd			
			14,873.'		14,875.'				
6713.4	14,891.	4vwd	14,892.	6vwd	14,894.	4vwd			
			14,910.'		14,917.'				
							15,661.	0wd	h
							15,694.	0wd	h
							15,726.'		
							15,762.	0vwd	
							15,809.'		
			15,825.	0d					h
			15,853.	2d	15,853.	0d	15,841.	0vfd	h
			15,880.	3d	15,881.	0d	15,877.	0vfd	h
6287.6	15,900.	6s	15,901.	5s	15,902.	0d			l
6276.6	15,928.	9s	15,928.	9s	15,928.	6d	15,923.		l
6265.6	15,956.	9s	15,956.7	9s	15,956.	6d	15,960.		l
			15,974.	0d					
			15,985.	0d					h
6248.9	15,998.	5d	15,998.	6d	15,998.	2vd	15,994.		
6234.4	16,036.	8d	16,036.	9d	16,035.	6d	16,037.		
6224.9	16,060.	7d	16,060.	8d	16,058.	4d	16,059.		t
			18,055.	1d					h
5514.0	18,131.	5d	18,129.	3d	18,131.	0d			l
5508.9	18,147.	1d	18,148.	1d					
			18,178.	0vd					h
5491.3	18,206.	2d	18,205.	2d	18,205.	0vd			
5486.4	18,222.	2d	18,225.	0d					
5475.1	18,259.	3s	18,259.	2d	18,260.	0d			
5470.1	18,276.	2d	18,276.	0d					
			18,304.	0d					h
5454.0	18,330.	2d	18,333.	2d					
5437.5	18,386.	1d	18,385.	1d	18,382.	0d			
5409.7	18,480.	1d	18,480.	1d					
			18,484.	2d					
5404.4	18,498.	1d	18,498.	2d	18,490.	0d			
5389.6	18,549.	0d	18,553.	1d	18,546.	0d			
5373.3	18,605.	0d	18,610.	0d	18,614.	0d			
			18,720.	0d	18,721.	2d			
			18,760.	2wd	18,761.	3wd	18,685.'		h
			18,805.	2wd	18,786.'				
					18,801.	4vwd			h
					18,818.'				
					18,830.'				
			18,845.	0wd	18,856.	2vwd			
					18,884.'				
			18,907.	0s	18,900.	1d			h
					18,925.'				
5277.3	18,944.	6s	18,946.	10d	18,947.	3vwd			h
					18,961.'				
					18,980.'				
5262.9	18,996.	6vs	18,996.	10wd	18,997.	2vwd			h
					19,014.'				
					19,020.'				
5255.9	19,021.	8ws	19,025.	10wd	19,030.	2wd			
					19,040.'				
5243.7'	19,065.'		19,057.'		19,052.'				
5242.1	19,070.	7vwd	19,085.	10	19,082.	2vwd			
5237.8'	19,087.'		19,113.'	vwd	19,123.'				
5228.8	19,120.	2s							
5226.9	19,127.	1s							
5224.2	19,136.	1s							
5223.3'	19,139.'		19,142.'		19,140.'				
5215.3	19,169.	6vwd	19,168.	9vwd	19,181.	2vwd			
5207.7'	19,197.'		19,195.'		19,224.'				
5206.3	19,202.	2d							
5203.7	19,212.	2d							
5200.9	19,222.	2d							
5198.8	19,230.	1d							
5195.2	19,243.	2d							
5187.7	19,271.	2d							
5185.8	19,278.	3d							
5177.6	19,309.	1d							
5174.6	19,320.	1d			19,265.'				
5164.4	19,358.	1d	19,369.	7d	19,327.	2vwd			h
5159.6	19,376.	0d			19,391.'				
5156.0	19,390.	1d							
5150.0	19,412.	1d							
5142.9	19,439.	6d	19,443.	8d	19,435.'				
5139.9	19,450.	8d							
5135.2	19,468.	0d							
5132.9	19,477.	0d	19,475.	7wd					
5120.7	19,523.	6wd	19,500.'						
			19,534.	8wd					
5112.8	19,553.	6wd	19,567.'			2vwd			

(298°K column marked *continuum* over lower portion of this half.)

Right half

Ångstroms (20°K)	Wave Number (20°K)	Int.	W.N. (78°K)	Int.	W.N. (169°K)	Int.	W.N. (298°K)	Int.	Type
5104.0	19,587.	5w					18,685.'		
5099.8	19,603.	5w							
5095.4	19,620.	5w							
5085.8	19,657.	3w							
5080.9'	19,676.'		19,678.'						
5068.8	19,723.	4vw	19,702.	7vwd					
5057.0'	19,769.'		19,727.'		19,753.'				
5052.0	19,789.	2d	19,790.	1d					
					19,834.'				
5046.1	19,812.	1d	19,855.'		19,875.	2vwd			h
			19,878.	3vwd	19,917.'				
			19,902.'						
5017.5'	19,925.'		19,936.'		19,935.		18,685.'		l
5012.1	19,946.	4dw	19,948.	3vwd	19,956.	2vwd			
5007.1'	19,966.'		19,971.'		19,978.'				
4994.0	20,019.	1d	20,024.	0d					
4981.7	20,068.	1d	20,069.	0d			20,054.'		
4973.8	20,100.	1d							
4962.9	20,144.	1d	20,138.	0d					
4836.6	20,670.	0d	20,670.	4s					
4824.9	20,720.	6vs	20,721.	8vs	20,724.	2d	20,713.'		
					20,756.'	1wwd			h
					20,787.'				
					20,824.'	0vwd			h
					20,875.'				
4774.2	20,940.	3s	20,939.	9d					
					20,951.	5wd			h
4770.2	20,957.	3s	20,957.	9d					h
4762.0	20,993.	4s	20,992.	9d					
					21,004.	5wd			h
4756.5	21,017.	8vs	21,017.	8s	21,036.	6d			l
4752.8	21,033.	8vs	21,033.	10s	21,069.	6d			l
4744.7	21,069.	8s	21,069.	8s	21,091.	6wd			l
4740.0	21,096.	8s	21,091.	8s					l
4730.7	21,132.	0d							
4727.3	21,148.	6dw	21,146.	8dw	21,131.'				
					21,147.	5vwd			
					21,153.'				
4716.0	21,198.	0d							
4714.0	21,207.	0d							
4711.9	21,217.	7d	21,218.	8d	21,215.	5d			
4707.8	21,235.	7vs	21,235.	4vs					
4705.9	21,243.	0vd	21,276.'		21,269.'				
4695.9	21,289.	6vwd	21,289.	7vwd	21,287.	6vwd			
			21,303.'		21,306.'				
4689.7	21,317.	0vd							
4684.9	21,338.	0vd							
4681.0	21,356.	0vd							
4673.3	21,392.	6vd	21,394.	7wd	21,395.	6wd			
4663.8	21,430.	0d	21,435.	1d					
4659.9	21,453.	2d							
4657.7	21,463.	8s	21,463.	8s	21,464.	4d			
4647.3	21,511.	6d	21,513.	3d	21,518.	2vd			
4638.8	21,551.	4wd	21,550.	3wd					
			21,568.'		21,570.'				
4631.9	21,583.	3vwd	21,583.		21,581.	2vwd			
			21,597.'		21,593.'				
4625.5	21,613.	4dw	21,615.	3dw					
4618.3	21,647.	2wd	too diffuse		21,643.	0vwd			
4605.9	21,705.	2dw	21,705.	2dw					
4586.9	21,795.	4dw							
			21,799.	3dw	21,800.	3dw			
4584.8	21,805.	2d							
			21,906.'		21,896.'				
4559.3	21,927.	4vwd	21,927.	7vwd	21,927.	2vwd			
			21,957.'		21,959.'		21,935.'		
4470.9	22,361.	0d							
4460.3	22,414.	2wd							
4456.0	22,435.	2d							
4447.7	22,477.	0vd							
4446.6	22,483.	0d							
4431.0	22,562.	1wd							
4424.3	22,596.	0d							
4411.1	22,664.	0d							
			23,045.	0d	23,043.	0d	23,014.	2d	h
							23,035.'		
			23,080.	4d	23,079.	4d	23,071.	6vwd	h
							23,109.'		
							23,221.'		
4303.5	23,230.	3s	23,229.	9s	23,229.	6s	23,233.	4d	h
							23,246.'		
							23,290.'		
4289.3	23,306.	9ws	23,305.	10ws	23,304.	8sw	23,310.	8vwd	l
							23,331.'		
4286.5	23,332.	2s							
4281.7	23,348.	4d	23,346.	2d					l
4279.8	23,359.	3s	23,356.	5s					
4278.8	23,364.	3s	23,368.	3s					
4277.7	23,371.	4s							

(298°K column marked *continuum* over portions of this half.)

tions that the field about the Nd ion has cubic symmetry and that there is L–S coupling in the ion's lowest state, they are able to account for the magnetic susceptibility data of Gorter and de Haas[4] over the temperature range 14° to 300°K. It is to be regretted that there are not more cryogenic susceptibility measurements for neodymium sulfate, especially since the magneton number given by Gorter and de Haas for 300° is notably different from the values found earlier by Meyer[5] and by Zernicke and James.[6]

While the theory is in excellent agreement with Gorter and de Haas' work on Nd it is not completely satisfactory for these reasons. (1) Crystallographically and chemically the octahydrated sulfates of the rare earths (always excepting Ce) are very closely similar and there can be little doubt that the lattice structures of all are the same. It follows that for all the rare earths the strength of the crystal field acting on a rare earth ion in its dependence upon direction and distance from the ion must be nearly the same. Especially is this true of adjacent elements. Penney and Schlapp have found, though, that in order to duplicate the susceptibility-temperature curves of Gorter and de Haas for $Nd_2(SO_4)_3 \cdot 8H_2O$ and $Pr_2(SO_4)_3 \cdot 8H_2O$ it is necessary to assume that there is about the metal ions a potential field whose constant D^7 for Nd is about four times as large as that for Pr. (2) According to Gorter and de Haas' data for $Nd_2(SO_4)_3 \cdot 8H_2O$, Nd^{+++}, whose normal state is $4f^3\ ^4I_{9/2}$, has a magnetic susceptibility which at low temperatures deviates sharply from the values calculated for the free (gaseous) ion, and which approaches the gas values only at relatively high temperatures. Er, complementary element of Nd in the second half of the rare

[4] C. J. Gorter and W. J. de Haas, Leiden Commun. 218 b.

[5] S. Meyer, Physik Zeits. **26**, 51, 478 (1925).

[6] J. Zernicke and C. James, J. Am. Chem. Soc. **48**, 2827 (1926).

[7] Penney and Schlapp write for the potential energy of an electron of a Pr or Nd ion in the electric field of the atoms which envelop it the expression $V = D(x^4+y^4+z^4)$. The field has cubic symmetry and the origin of coordinates is taken as the center of the rare earth ion.

TABLE I.—*Continued.*

20°K			78°K		169°K		298°K			20°K			78°K		169°K		298°K		
Ang-stroms	Wave Number	Int.	W.N.	Int.	W.N.	Int.	W.N.	Int.	Type	Ang-stroms	Wave Number	Int.	W.N.	Int.	W.N.	Int.	W.N.	Int.	Type
4269.2	23,417.	0wd								4000.6	24,989.	5s	24,990.	0d					
4264.4	23,444.	0wd											26,101.	5s	26,101.	3d	26,114.	1d	h
4257.4	23,482.	0wd								3818.9	26,178.	10vs	26,178.	9s	26,178.	7s	26,184.	3d	l
4244.7	23,552.	0d								3804.7	26,276.	10s	26,274.	5s	26,272.	3d	26,272.	1d	
4238.0	23,590.	0d																	
4234.4	23,609.	0d								3751.6	26,648.	6vs	26,648.	2s	26,654.	1d			
4228.3	23,644.	5s	23,645.	2s						3747.4	26,678.	3s	26,676.	4s					
4223.5	23,670.	4d	23,672.	0d															
			23,684.	4d	23,685.	0d			h	3741.7	26,718.	9vs	26,717.	4s	26,720.	2d	26,731.	0d	
4211.4	23,738.	3d	23,735.	0d						3739.7	26,732.	1s							
4207.3	23,762.	10vs	23,761.	10s	23,759.	6d	23,765.	3d	l	3736.8	26,753.	0s							
			23,806.	0d	23,812.	0d			h	3624.4	27,583.	1d	27,587.	1d	27,589.	0d			
4186.8	23,878.	5d	23,883.	0d	23,885.	0d			l	3621 9	27,602.	0d							
4181.6	23,908.	1d								3619.3	27,622.	3s	27,623.	2d					
4177.5	23,931.	3s								3614.9	27,655.	5s	27,655.	4d	27,659.	0d			
4175.5	23,943.	7sw	23,947.	1d	23,946.	1d				3604.8	27,733.	1d	27,737.	1d	27,738.	3d			
4173.2	23,956.	8s	23,954	0d									27,782.	2d	27,783.	3d			h
4169.2	23,979.	2d											27,817.	3d	27,815.	5d			h
4163.5	24,012.	1d											27,944.'						
4153.0	24,072.	4s	24,073.	0d						3574.3	27,969.	10vs	27,973.	8vwd					
4145.3	24,117.	6d	24,121.	0d	24,126.	0d							27,992.'						
4070.3	24,562.	8vs	24,562.	3s	24,564.	0d	24,572.	0d					28,019.'						
4056.9	24 642.	1s								3564.7	28,045.	10sw	28,044.	8vwd					l
4054.7	24,656.	1s											28,069.'						
4050.8	24,680.	0s											29,019.	4s	29,024.	3s			
							24,772.	0d					29,039.	0s					
4020.5	24,865.	10s	24,866.	7s	24,862.	3d	24,879.	2d		3438.4	29,075.	3s	29,074.	1s					
4010.2	24,929.	4s	24,932.	0d						3435.7	29,098.	10vs	29,099.	6s	29,099.	5wd			
4007.9	24,944.	9vs	24,944.	2s	24,947.	1d							29,326.	2d					
4006.2	24,954.	7s	24,954.	1s									29,348.	0d					
4003.8	24,969.	7s	24,971.	1d	24,968.	1d	24,966.	0d		3401.5	29,391.	0dw	29,401.	3d	29,405.	0d			
4002.3	24,979.	3s																	

w = 15–30 cm^{-1} width.
vw = more than 30 cm^{-1} width.
vs = very sharp, very well defined line.
s = sharp, well defined line.
d = diffuse, poorly defined.
vd = very diffuse, very poorly defined line.
h = high temperature line (see text).
l = low temperature line (see text).

The intensities given are visual approximations made by the author for each plate on a scale of 0–10. 0 intensity was too faint to be seen under the comparator, and the plate had to be scratched to measure. 1 intensity was very faint and was also scratched, 2–5 intensity were rather faint, and 5–10 strong absorption, 10 being complete in the center of the line or band. The probable errors of the lines designated as sharp are: 0 and 1 intensity about 5 cm^{-1}, 2 and 3 about 3 cm^{-1}, 4–6 about 1 cm^{-1}, 6–10 about 0.5 cm^{-1}. The probable error of the diffuse lines are: (0 and 1) intensity about 10 cm^{-1}, 2–5 about 5 cm^{-1}, 6 and 7 about 3 cm^{-1}, 8–10 about 2 cm^{-1}. This error will of course depend on the position of the lines on the plate.
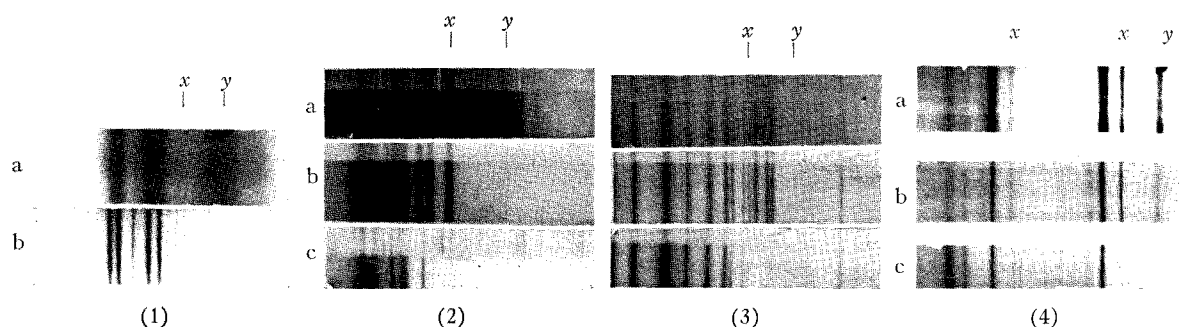
FIG. 1. (1) Multiplet at 16,000 cm^{-1}. Prism spectrograph a, 300°K, b, 78°K. (2) Multiplet at 19,000 cm^{-1}. Grating spectrograph. (3) Multiplet at 21,000 cm^{-1}. Grating spectrograph. (4) Multiplet at 23,300 cm^{-1}. Grating spectrograph. a, 169°K, b, 78°K, c, 20°K. x, lines originating at the 77 cm^{-1} level. y, lines originating at the 260 cm^{-1} level.

earth group, also has a ^4I normal state in its salts. Susceptibility measurements of $Er_2(SO_4)_3$ $\cdot 8H_2O$ by de Haas, Wiersma and Capel[8] indicate almost perfectly gas-like behavior for Er^{+++} over the entire temperature range 14°–285°K.[9] In view of the similarity of the two elements, if the theory is made to agree with the data for Nd it is not to be expected that it will agree with that for Er.[10] (3) Although the normal state of Sm^{+++}, $^6H_{5/2}$, may split into only two states in a cubic field (into three in a field of lower symmetry) at least four low levels besides the normal one have been found spectroscopically.[11] (4) In the theory of the susceptibility of Nd^{+++} a crystal field of predominantly cubic symmetry is assumed and the attempt to substitute for it a predominantly rhombic field has been definitely unsuccessful. Since the crystallographic symmetry is monoclinic it might be expected that there would be less than cubic symmetry about the Nd ion. From this it follows that the field about the rare earth ion is determined almost entirely by its envelope of oxygen atoms situated, presumably, at the corners of an octahedron not appreciably distorted by the sulfate ions (which very likely furnish some of the oxygen atoms since enough of them are not provided by water molecules alone).

[8] W. J. de Haas, E. C. Wiersma and W. H. Capel, Leiden Commun. 201 b.

[9] Something seems to be wrong with at least the absolute values of the susceptibility of $Er_2(SO_4)_3\cdot 8H_2O$, for the magneton number of 44.8 at room temperature reported by de Haas, Wiersma and Capel is very much smaller than the most probable one, 47.3, given by Gorter (Dissertation, Leiden, 1932). A repetition of the Er measurements has been promised.

[10] Spedding, Phys. Rev. **50**, 574 (1936).

[11] F. H. Spedding and R. S. Bear, Phys. Rev. **46**, 975 (1934).

In view of the shortcomings of the susceptibility theory a spectroscopic investigation of the energy states of $Nd_2(SO_4)_3\cdot 8H_2O$ is of particular interest.

EXPERIMENTAL PART

The work was begun at the University of California where one set of plates of the absorption spectrum of neodymium sulfate was obtained at each of the following temperatures, 20°K, 78°K, 169°K, 300°K. A complete description of the apparatus and procedure has been given already.[12] The salt was used in the form of conglomerates of small crystals and the thickness was from 3 to 5 mm. The origin of the neodymium is unknown but its purity is adequate for the only foreign substance present in detectable amount is Pr, whose strongest absorption lines show faintly in the spectra of thick conglomerates.

A second series of spectra was photographed at the temperatures 78° and 300°K with the large glass single prism spectrograph of the chemistry department of Cornell University. The dispersion is such that the visible spectrum is spread over about 20 cm. The procedure was exactly the same as at California. The neodymium used was some which Dr. H. N. McCoy very generously presented to one of us to further research along these lines. It is of somewhat better purity than that used at California. All the plates were measured on the large comparator belonging to the Cornell physics department.

[12] F. H. Spedding and R. S. Bear, Phys. Rev. **42**, 58 (1932); F. H. Spedding and G. C. Nutting, J. Chem. Phys. **2**, 422 (1934).

The accuracy of measurement, of course, varies greatly since it depends upon the sharpness of the lines and their intensity, the temperature at which the spectra were photographed, and the region of the plate. We think that in general the positions reported for the sharpest lines in the most favorable region of the plate are correct within 0.2 cm^{-1}, while in the case of the weak, diffuse bands the error may be as much as 20 cm^{-1}. For most lines the error is probably not more than 2 cm^{-1}. Many of the lines and bands are so faint that they are invisible under the magnification of the measuring engine, hence their positions were marked by fine scratches in the gelatine made by a needle with the aid of a low power eyepiece.

Data giving the position, intensity and character of the lines is presented in Table I. From these data a rough estimate of the accuracy of individual measurements may also be obtained. The intensities have been gauged visually on the scale 0–10 and are principally useful in estimating relative intensities of adjacent lines. Even here they are valid only for a conglomerate of given thickness and particle size because[13] in a photograph of the absorption spectrum of a conglomerate the frequencies weakly absorbed appear relatively more prominently than the ones strongly absorbed.

The existence of excited levels lying close to

TABLE II. *77 cm^{-1} levels.*

	78°K	
1	h	Δv
14,737.	−14,658.	79.
14,700.	−14,622.	78.
15,901.	−15,825.	76.
15,928.	−15,853.	75.
15,956.7	−15,880.	76.7
16,060.	−15,985.	75.
18,129.	−18,054.	75.
18,259.	−18,178.	81.
18,384.	−18,304.	80.
19,025.	−18,946.	77.
19,071.	−18,996.	75.
19,443.	−19,368.	75.
19,955.	−19,879.	76.
21,017.	−20,939.	78.
21,033.	−20,957.	76.
21,069.	−20,992.	77.
23,305.	−23,229.	76.
23,761.	−23,684.	77.
23,883.	−23,806.	77.
26,178.	−26,101.	77.

[13] F. H. Spedding and R. S. Bear, Phys. Rev. **39**, 948 (1932).

the basic state has been determined by two independent methods. The first takes advantage of the fact that the intensity of absorption is proportional to the number of absorbers in the lower state. This in turn is determined by the absolute temperature according to the Boltzmann relation. All lines originating at a given excited state must fade out with more or less suddenness as the temperature is lowered beyond a certain point, and from this temperature one can calculate roughly the separation of the normal and the excited states. Fig. 1 shows several examples of this phenomenon.

The second method depends upon the fact that if absorption lines arising from two lower levels and terminating in a variety of common upper levels occur in the spectrum, a constant frequency interval equal to the separation between the lower levels is found repeatedly throughout the spectrum. An excited lower level of neodymium sulfate 77 cm^{-1} above the normal one has been discovered in this way and the best evidence for it is listed in Table II.

By means of the first method it is established beyond doubt that at least one level must exist between 250 and 300 cm^{-1} (see Fig. 1). It is unfortunate that transitions beginning at this excited level are infrequent until the temperature of the crystal is rather high. The corresponding absorption lines are then usually so wide and so diffuse that their positions cannot be measured with high accuracy. A further complication is introduced by the fact that the levels comprising the multiplets of the upper state most often are so close together that at the temperatures in question thermal broadening as a rule causes the absorption lines to fuse. This makes it very

TABLE III. *260 cm^{-1} levels.*

	78°K	Δv
15,661 (*RT*)	−15,923 (*RT*)	262
15,694 (*RT*)	−15,960 (*RT*)	266
18,760	−19,025	265
18,805	−19,070 (*h*)	265
18,907	−19,168	261
{ 20,787 (*e*)	−21,033 }	*s* 260
{ 20,756	−21,017 }	
{ 20,824	−21,091	*s* 260
{ 20,875		
23,045	−23,305	260
23,080	−23,346	266
27,782	−28,044	262

s =about, *h* =20°K, *e* =169°K, *RT* =300°K.

unusual to find clear cases of constant energy differences. There are, however, a few such cases in which Δv is about 260 cm^{-1} and this separation accounts for all the instances discovered solely by Method I within our limits of error of estimation (Table III).

The spectra resemble in a general way those reported earlier for Sm.[12] The absorption lines are grouped in multiplets which are scattered through the visible and near ultraviolet. In the case of Nd there are fewer multiplets than were found for Sm, and these usually have more lines.

14,700 cm^{-1} multiplet

This prominent group is typical of a number of such groups to the extent that its lines are diffuse and wide even at 20°. The lines are almost certainly complex and have not been resolved due either to lack of a sufficiently low temperature or more probably due to a broadening of the levels brought about by the neighboring atoms in the solid. Lines arising from the 77 cm^{-1} level appear associated with the two intense long wave-length lines of the multiplet. Whether or not high temperature lines[14] are associated with other intense low temperature lines cannot be determined from our data since the low temperature lines are so spaced that they lie where the high temperature lines are expected to occur, thus masking them if they do exist. It is true in general that high temperature lines can be distinguished clearly only at the long wave-length edge of a multiplet, for the upper levels are usually so close together that high temperature lines in the body of a multiplet fall on or near the long wave-length components of the multiplet arising from the normal state.

15,900 cm^{-1} multiplet

The lines of this multiplet are unusually intense. Several of them originate at levels 250 cm^{-1} or more above the normal one and in the case of two pairs of lines measurable with somewhat greater precision than the rest the separation is close to 260 cm^{-1}. In this as in most of the multiplets there is positive evidence for the existence of the 77 cm^{-1} level.

17,500 cm^{-1} multiplet

General absorption apparently underlies the discrete structure making accurate measurements impossible. Many lines present are not being reported because of their excessive faintness, diffuseness and lack of resolution. Likewise evidence for the 77 cm^{-1} and 260 cm^{-1} levels is being withheld because of its too great degree of uncertainty. A second unfortunate circumstance is that the

junction of the grating plates has usually chanced to occur within this multiplet.

18,250 cm^{-1} multiplet

The absorption in this multiplet also is extremely weak and therefore very difficult to measure. At 169° and above it is scarcely visible.

19,000–19,600 multiplets

These are two of the most intense multiplets in the spectrum. The strong components, most of which are diffuse, overlay a background of fainter lines that sometimes are so little separated from their strong companions as to make correct measurement of the position of the latter doubly difficult. Here again there is a considerable amount of evidence for excited levels at 77 and 260 cm^{-1}.

In the region between *17,500 and 23,000 cm^{-1}* there is an almost continuous succession of very faint lines which in the main are probably attributable to Nd but which in some cases may be due to impurities. Superimposed upon this background are the intense multiplets which we have measured. At frequencies higher than 23,000 cm^{-1} are a number of groups of well-defined lines which further substantiate our assertion that there is a level at 77 cm^{-1}.

DISCUSSION OF RESULTS

Hund[15] predicted the character of the normal states of the rare earth ions in solid salts, assuming the validity of the usual coupling rules for gaseous atoms. He then computed the magnetic susceptibilities of the ions, supposing that only the normal states contribute appreciably toward their paramagnetic properties. Agreement with the experimental values for temperatures of 300°K and higher is good for all the rare earths except Sm and Eu. Frank[16] has shown that very important corrections, due to the contribution of the other levels of the normal multiplet and especially due to interaction among the lowest levels, must be added to the Hund values for Sm and Eu. Corresponding corrections for Nd amount to only about three percent, and for our purpose may be neglected.

In Hund's work it is implicit that the interaction energy of J with the crystal field is always small compared with kT, and while the assumption is clearly justified by experiment at room temperature and above, it is expected and is often found to be invalid at low temperatures. Penney and Schlapp have been able to predict

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[14] By low temperature lines we mean those originating at the normal state and by high temperature lines those originating at the excited lower states.

[15] F. Hund, Zeits. f. Physik **33**, 855 (1925).
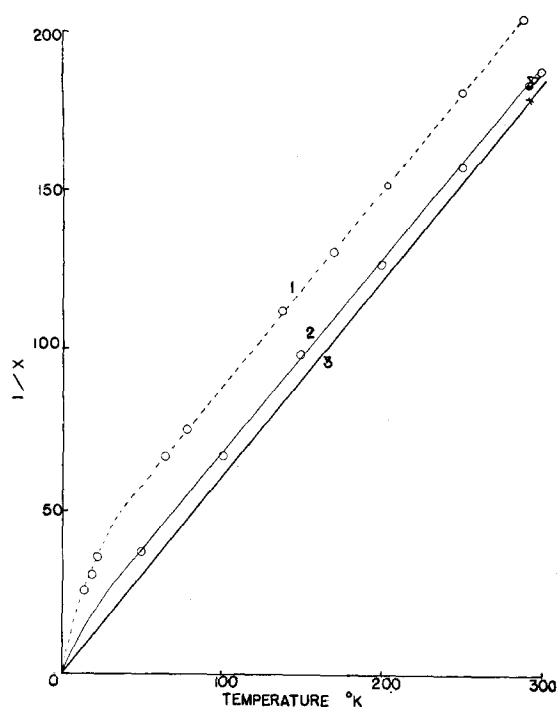[16] A. Frank, Phys. Rev. **39**, 119 (1932).

FIG. 2. (1) o Gorter and de Haas' experimental points. - - - Penney and Schlapp's theoretical curve. (2) -o-o Penney and Schlapp's theoretical curve using our levels. (3) Hund's curve. o△, Meyer and Zernicke and James experimental points. X, Cabrera's experimental point.

the relative position of the three levels of Nd^{+++} produced by splitting of its normal state in a crystal field of cubic symmetry, and of the ten levels which result from superposition of a magnetic field upon the crystal field. In order to determine the actual Δv's recourse to experiment must be had, and from extrapolation of measurements of Gorter and de Haas, Penney and Schlapp have determined the over-all separation of the multiplet in the absence of a magnetic field to be 834 cm^{-1}. It then follows from their own work that the intermediate level is 243 cm^{-1} above the lowest one. As has been said earlier the calculated variation of susceptibility with temperature for Nd$_2$(SO$_4$)$_3 \cdot$8H$_2$O agrees very closely with that measured.

Our findings are in definite disaccord with these predictions. In addition, using our spectroscopically determined levels, we are not able to reproduce the experimental temperature-susceptibility curve by any known relationship between susceptibility and energy states. If we may assume that the susceptibility measure-

ments of Gorter and de Haas are in some measure incorrect and that the multiplet interval 834 cm^{-1} deduced from those measurements is likewise incorrect, we discover that our results are in excellent agreement with Penney and Schlapp's conclusions. The relative positions of the multiplet levels which they suggest and which are expressed by the numbers 0, 243 and 834 are virtually identical with those we have found at 0, 77 cm^{-1} and 260 cm^{-1}. The assertion (based on the data of Gorter and de Haas) that the crystal field has predominantly cubic rather than predominantly rhombic symmetry is likewise substantiated. Splitting of the "cubic" levels by a field of rhombic symmetry would have an inappreciable effect on the susceptibility so long as the amount of the splitting is small compared with that produced by the cubic field, but it should be easily detected spectroscopically. In Fig. 2 are presented plots of magnetic susceptibility vs. temperature for Nd$_2$(SO$_4$)$_3 \cdot$8H$_2$O as calculated by Hund, as measured by Gorter and de Haas, and as calculated by means of the equation of Penney and Schlapp, using our data. This last plot has less curvature than that of Gorter and de Haas and more closely resembles that for the free gaseous ion given by Hund. It is, furthermore, in agreement with the experimental values of the susceptibility at room temperature found by Meyer and Zernicke and James.[17] The curve is more nearly of the type of that for erbium, so that one objection mentioned in the introduction is thus removed.[10] This phase of the problem will be discussed in detail in a later paper on erbium. Finally, the field constant D is only one-third as large as that calculated by

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[17] The experimental work in this field is not at all satisfactory as the various investigators do not agree among themselves. Thus Selwood, J. Am. Chem. Soc. **55**, 3161 (1933), gives the following summary of values at room temperature for Nd$_2$(SO$_4$)$_3 \cdot$8H$_2$O:

	Specific Susceptibility $\times 10^6$
Wedekind	14.5
S. Meyer	14.6
Cabrera	15.4
Zernicke and James	14.5
Gorter and de Haas	13.08
Selwood	14.6

Selwood's results at liquid-air temperature, however, do not agree with our calculated ones nor do they agree with the experimental ones of Gorter and de Haas. Recently Jackson, Proc. Phys. Soc. (Sept. 1936), stated his results check Gorter and de Haas' within the experimental error but is not very specific as to the magnitude of his errors.

Penney and Schlapp[18] and has almost the same value as the constant they give for Pr (which, incidentally, may not be quite right for the magneton number of $Pr_2(SO_4)_3 \cdot 8H_2O$ determined by Gorter and de Haas is appreciably different from those reported by other investigators).

The anomaly of samarium, which was referred to in the introduction, remains, supporting Spedding's contention that there must be in

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[18] Professor Van Vleck writes us the following comments regarding the determination of the field-constant D from the experimental data of Gorter and de Haas on $ND_2(SO_4)_3 \cdot 8H_2O$. "As suggested by Dr. Gorter, the value of D is much less sensitive to errors in calibration if based exclusively on the measurements at very low temperatures rather than primarily on the absolute susceptibility at room temperatures as in the original paper of Penney and Schlapp. When T is sufficiently low, the susceptibility should theoretically obey a formula of the form $X = AT^{-1} + B$, and such an expression is approximately satisfied by the Leiden data below 20°K. As Gorter points out, a determination of D entirely independent of calibration is obtained from the experimental value of B/A if one assumes that A has the theoretical value corresponding to $1.83(8/11) \cdot \sqrt{3} = 2.3$ Bohr magnetons. By this method, a value of D is found which is 6 percent lower than that found by Penney and Schlapp for $Pr_2(SO_4)_3 \cdot 8H_2O$. At first sight it thus appears that the glaring discrepancy between Pr and Nd by a factor 3.9 as reported by Penney and Schlapp is removed, but unfortunately the experimental value of A does not check with theory, and yields a magneton number only 1.7. It is entirely inconceivable that the calibration error is as great as a factor $(2.3/1.7)^2$, and if A corresponds to a magneton number only 1.7, the value of D for $Nd_2(SO_4)_3 \cdot 8H_2O$ is 80 percent greater than for $Pr_2(SO_4)_3 \cdot 8H_2O$. Much more serious than this discrepancy, however, is the fact that the experimental data on A yield a magneton number so much lower than the minimum possible value 2.3 for a cubic field. This difficulty was not mentioned in the Penney and Schlapp article, and casts doubt on either the adequacy of the simple crystalline potential model or else on the cubic character of the crystalline field."

Sm^{+++} an extra electronic level which lies near the normal state. There is no doubling of the levels of Nd^{+++} as in the case of Sm^{+++} and thus the view of Van Vleck and Frank that the supernumerary levels are of vibrational origin seems unlikely to be correct. Owing to the close similarity of corresponding salts of different rare earths it does not appear probable that a vibrational level should occur in Sm and not in Nd or Gd, elements on either side of it in the periodic table.

Just as in the instance of Sm a measurement of the heat capacity of $Nd_2(SO_4)_3 \cdot 8H_2O$ in the range 14°–300°K would be of interest. Chemically and crystallographically the rare earth sulfate octahydrates are so nearly alike that their vibrational and lattice frequencies should be the same except for mass corrections. Considering the pair of salts $Nd_2(SO_4)_3 \cdot 8H_2O$ and $Gd_2(SO_4)_3 \cdot 8H_2O$, since the molecular weights differ by less than 4 percent the mass correction should be very small. Any difference in the heat capacity of the salts should then be due to differences in their electronic states. The normal state of Gd^{+++} is single so that the curve of the heat capacity difference between the Gd and Nd salts plotted against absolute temperature should show humps at the temperatures at which the 77 and 260 cm^{-1} levels of Nd^{+++} become appreciably populated.