1941

A study of the absorption spectra of some neodymium compounds

John Frank Palmer Jr.
Iowa State College

Recommended Citation

Palmer, John Frank Jr., "A study of the absorption spectra of some neodymium compounds " (1941). *Retrospective Theses and Dissertations*. 12947.
https://lib.dr.iastate.edu/rtd/12947

A STUDY OF THE ABSORPTION SPECTRA OF SOME NEODYMIUM COMPOUNDS

by

John F. Palmer, Jr.

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

1941

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

CONTENTS

I. INTRODUCTION

Nearly all of the physical and chemical properties of an atom except those properties depending upon mass are determined by the energy states of the outermost or valence electrons and how they behave in various fields. For example, isotopes differ from one another only in mass, having identical other properties since their electron shells are exactly alike. On the other hand isobars, although their internal structures and masses are identical, differ radically due to different valency shells.

If for the atoms of a substance all the energy states were known and their various behaviours to electric and magnetic fields, caused by the approach of neighboring atoms, were understood, it would be possible to predict the chemical and physical properties of the substance. This state of affairs is far from being attained as yet but much progress has been made in that direction. In the case of gases good correlations have been made between the spectra and properties such as: specific heat, magnetic susceptibility, dielectric constant, electrical conductivity, refractive index, optical activity, heats of formation, entropy, free energy, fugacity, etc.

In the case of solids, liquids, and solutions unfortunately, the absorption spectra at room temperature consist of very broad diffuse bands. However, if sufficiently low temperatures are obtained some of these bands become sharp and resemble the gas type spectra while others are not appreciably changed. Happily, theory definitely predicts which bands will show a temperature sharpening and which will not.

It is rather unfortunate that all liquids and solutions become solid at the temperature at which most lines are resolved. At higher temperatures changes in the positions of the neighboring atoms due to temperature motion cause the electric and magnetic fields on the central atom to vary. This gives rise to a crystalline "Stark" or "Zeeman" splitting of the energy levels of that atom. The spacing and position of the absorption lines arising from these levels will vary with the momentary fields. The absorption spectrum observed on a photographic plate is the integrated absorption caused by millions of atoms and if the temperature motion is large the absorption lines will be blurred into broad bands. In the rare earths these temperature effects are minimized by the shielding effect of the outer complete electron shells in the rare earth ion and this results in the absorption lines still remaining sharp at liquid air temperatures. The rare earths are typical trivalent ions. Therefore, a study of their energy states as determined from spectra would furnish ideal data upon which to test theories.

The absorption spectra of solids are much more complex than those of gases. This is because the atoms are subjected to fields of much lower electric and magnetic symmetry. In gases the fields are spherically symmetrical since they arise entirely from the atom concerned and this gives rise to considerable degeneracy of the levels. The lower symmetry of the fields of the solids partially removes this degeneracy and causes the gas levels to separate into several components. As a result more components appear in the spectra. On the other hand this greater complication permits more correlations due to the greater number of variables. At present the experimental data on the spectra of gases are very extensive, while those on solids are extremely meager. Accordingly good data are urgently needed for the correlation of chemical and physical properties in the case of solids and solutions.

This research was undertaken in order to make available a greater amount of good experimental data to check future theoretical work. Some examples of present theory will be checked herein to show how the data can be used.

It is also hoped that results of this sort will furnish experimental values from which forces acting within a solid and their variance from point to point can be calculated.

II. PREVIOUS INVESTIGATIONS

A. Spectroscopic

Spectroscopic investigations of the rare earths date from Bunsen's work (1) on the absorption spectra of solutions and crystals of salts of "didymium", a mixture of neodymium and praseodymium. About forty years later, Jean Becquerel and co-workers at Leiden undertook the study of the absorption spectra of certain minerals which contained mixtures of rare earth salts. In the course of their investigations they found that by lowering the temperature of the sample the absorption lines became sharper (2). Temperatures as low as that of solid hydrogen (12° K.) were used. These investigators also studied the effect of a strong magnetic field on the absorption bands of "didymium", etc. These workers did not confine themselves to any one specific ion and their measurements were limited on the short wave length side by the glass vessels which surrounded their samples.

Freed and Spedding, in a communication (3) to Nature of April 6, 1929, announced the beginning of a systematic investigation of the absorption spectra of solids which has been continued up to the present time by these and other workers. For the initial investigations the gadolinium ion was chosen since its spectra would presumably be the simplest because its basic electronic level $^8S_{\frac{7}{2}}$ is single. The spectrum, which lay almost entirely in the ultraviolet region except for a few faint diffuse lines in the visible, consisted of extremely sharp lines (4) even at room temperature. As the temperature was lowered the lines sharpened slightly and a slight shift toward longer wave lengths together with a greater separation between lines composing each group was noted. These effects they attributed to the thermal contraction of the crystal lattice which consequently intensifies the electrostatic fields surrounding the cation.

About this time, the theoretical physicist, Bethe (5), using the methods of wave mechanics and group theory, investigated the influence of a crystal field of various symmetry on an atom. He concluded that the energy level splitting is determined by the symmetry of the field and the total angular momentum of the atom. In general, s-terms do not split, and p-terms do not split in a cubic field. Bethe calculated the eigen function for each term in a crystal to a zero order approximation. For each term the characteristic grouping of electron density about the axes of symmetry of a crystal was determined. The magnitude of the term-splitting is of the order of a few hundred inverse centimeters. He also found that with a crystal with tetragonal symmetry there is obtained a quantitative measure of the departure from cubic symmetry which determines uniquely the most stable electron arrangement in the crystal. Quantum mechanics is in qualitative agreement with the experiments of Becquerel (6).

Working with the reflection spectra of $SmCl_3.6H_2O$, Spedding and Bear (7) observed, as had others previously, that the use of a conglomerate of small crystals in place of a large single crystal resulted in the appearance of new absorption lines and the strengthening of others. This they explained as being caused by the increased length of path travelled by the light which is partially absorbed rather than an effect due to surface atoms as previously considered. The increased path results from the high refractive index for the light of wave length of the absorption lines, thus making it difficult for such a ray, once it has entered a small crystal fragment, to leave.

Spedding and Bear next published a series of papers(8) on the absorption of the Sm^{+++} ion in solids. Using large single crystals, the spectra of $SmCl_3 \cdot 6H_2O$ were photographed at seven temperatures between 15 and 298°K. They were measured at four of the temperatures. All phenomena observed were explained on the basis of three direct effects of temperature change on the crystal lattice:

(a) lattice contraction and expansion,

(b) temperature vibration of the lattice with consequent fluctuations in the crystal fields,

(c) Boltzmann distribution of the ions between excited lower levels about 160, 210 and 300 $cm.^{-1}$ above the basic level.

Work on the conglomerate yielded additional lines and established the existence of excited lower levels situated at 145, 160, 204, 217 and 300 $cm.^{-1}$ above the basic level. Two components of the 300 level are thought to be present, and there are indications that the other levels, especially the basic one, may be complex.

Selection rules were indicated for $Sm(BrO_3)_3 \cdot 9H_2O$ which show two apparently independent sets of levels:

(a) 0, 37, 82 and one group of high levels,

(b) 0, 45, 67 and another group of high levels

This low-temperature splitting was attributed to either actual removal of degeneracy or to development of two types of Sm^{+++} ion, caused by a crystalline modification and differing in crystal environments. In contrast to the less symmetrical (monoclinic) chloride, the hexagonal bromate showed less extension and complexity of upper multiplets and had the excited lower levels closer to the basic level.

Continuing this work, the same authors found the following levels for other salts of samarium:

(a) ethyl sulfate: 0, 55 and 65 $cm.^{-1}$

(b) iodide: 0, 90 and 107 $cm.^{-1}$

(c) perchlorate: 0, 104 and 160 $cm.^{-1}$

(d) sulfate: 0, 160, 188 and 225 $cm.^{-1}$

It was suggested that crystal splitting of the basic $^6H_{5/2}$ level could not account for all the levels, since only three new levels $(J + 1/2)$ can be expected when electric perturbations remove the degeneracy of such a state.

Spedding and Nutting, extending the work on salts of gadolinium (9), made measurements on the spectra of the bromate, ethyl sulfate, nitrate and sulfate. In these spectra a very marked change was noticed in going from the monoclinic symmetry of the chloride, bromide and sulfate to the hexagonal symmetry of the bromate and ethyl sulfate. The higher the degree of symmetry, the smaller the separation of levels. The absorption spectra of the gadolinium ion consists of lines which arise from electronic transitions from a single basic level ($4f^7$, $^8S_{7/2}$) to excited levels which are less-degenerate through the influence of the electric fields of neighboring atoms.

The neodymium ion has likewise been worked on. Ephraim and Ray measured the reflection spectra of neodymium oxide (10) and reported thirty-five band peaks in the visible. The absorption spectra of hydrated neodymium sulfate at 20, 78, 169 and 298°K., and of hydrated neodymium chloride at 78, 169 and 200°K. were examined by Spedding, Hamlin and Nutting (11). For the sulfate, the levels 0, 77 and 260 $cm.^{-1}$ were found. These values are not in quantitative agreement with the theoretical conclusions of Penney and Schlapp (12), which were based on the experimental work of Gorter and de Haas (13) and require levels at 0, 243 and 834 $cm.^{-1}$. If the work of Gorter and de Haas is in error as regards absolute values, the positions found by Spedding and co-workers are in excellent agreement with the theories of Van Vleck (14) and of Penney and Schlapp. In addition they agree with the experiments of Meyer (15) and of Zernicke and James (16), which also disagree with the absolute values of Gorter and de Haas. In the case of the chloride, the levels were 0, 62 and 250 $cm.^{-1}$, which presumably arise from the splitting of the $^4J_{9/2}$ basic state of neodymium ion in a predominantly cubic field.

Ewald (17) examined the sharp absorption lines of the following salts of neodymium: zinc-neodymium double nitrate, magnesium-neodymium double nitrate and the nitrate, sulfate, chloride and bromate. From his rather meager data he concluded that the following levels were present:

(a) zinc-neodymium nitrate: 0, 36.6 $cm.^{-1}$

(b) magnesium-neodymium nitrate: 0, 33.6 $cm.^{-1}$

(c) neodymium nitrate: 0, 30.2 $cm.^{-1}$

(d) neodymium sulfate: 0, 77 $cm.^{-1}$

(e) neodymium chloride: 0, 61.5 cm.$^{-1}$

(f) neodymium bromate: 0, $\sim$ 115 cm.$^{-1}$

Also for each salt he states that there is a third level between 200 and 300 cm.$^{-1}$.

The splitting of the basic state of hydrated erbium sulfate due to the presence of the crystalline fields was now calculated by Spedding (18) according to the methods of VanVleck and Penney and Schlapp (loc. cit.). Assuming a cubic field, the basic state should split into five levels having the relative separations 0, 19, 39, 85 and 89 cm.$^{-1}$. Experimentally Meehan and Nutting have found 0, 19 , 41 and 85 cm.$^{-1}$ (19). The agreement with magnetic susceptibility data was also very good.

In the case of the praseodymium ion, Spedding, Howe and Keller obtained the absorption spectra of hydrated praseodymium sulfate at 20, 78, 105, 169, 200 and 300^{o} K. Low lying excited levels were found at 0, 110, 235 and 500 cm.$^{-1}$ in fair agreement with the calculations of Penney and Schlapp (loc. cit.). A very strong coupling of vibrational states with the highly excited energy states seems to occur as the absorption bands consist of hundreds of closely spaced fainter lines. Two methods were used for identifying the levels:

(a) The intensity of absorption is porportional to the number of atoms in the lowest state, which is in turn proportional to the temperature according to the Boltzmann relationship. As the temperature is lowered, a critical point is reached where the lines from the lowest state fade out.

(b) Since lines originating from lower states terminate in common upper states, the interval of the lower states will be repeated throughout the spectra.

Gobrecht studied the visible and infra-red absorption spectra (21) of the octahydrated sulfates of many of the rare earths at the temperature of liquid air. In the case of the four fluerescent elements Sm, Eu, Tb and Dy, the emission spectra in borax beads were also examined. These emissions were attributed to transitions from a higher state to the complete multiplet of the ground state as given by the Hund rule (22).

A study of the crystal fields of the europium ion, making use of both absorption and emission spectra has been made by Lange (23). The europium ion is especially suited for this work since the upper state, from which the emission starts, is either an S-state or has an inner quantum number $J = 0$ and is therefore not split. The acetate, nitrate, sulfate, oxalate, phosphate, double magnesium nitrate and bromate were used. The spectra were displaced about 10 cm.$^{-1}$ to the red at -180° C.

Continuing the work on europium Spedding, Moss and Waller (24) measured the absorption spectra of crystalline, hydrate europium chloride, bromide and sulfate at various temperatures. The salts were found to have low-lying excited levels at about 300, 390, 938, 970 and, perhaps, 430 cm.$^{-1}$ which arose from excited electronic, crystal and vibrational frequencies. Good agreement was also found with magnetic susceptibility data.

B. Magnetic

The German theoretical physicist Hund, in 1925, published a paper (22) in which he calculated values for the magnetic susceptibilities of all the rare earth ions from a few simple postulates on the quantum numbers of the basic electronic orbits. Experimentally determined values of Cabrera (26) and St. Meyer (15) were in agreement with his work. The facts are probably best presented by the following table taken from Hund's paper:

Table I. Comparison of theoretical and experimental magnetic data

Element	No. of 4f electrons	Ground state	Calcu. no. of Weiss magnetons	Experimental no. of Weiss magnetons	
				Cabrera	St. Meyer
La^{+++}	0	$^1S_0$	0	----	diamagnetic
Ce^{+++}	1	$^2F_{5/2}$	12.5	11.4	13.8
Pr^{+++}	2	$^3H_4$	17.8	17.8	17.3
Nd^{+++}	3	$^4I_{9/2}$	17.8	18.0	17.5
Il^{+++}	4	$^5I_4$	13.4	----	----
Sm^{+++}	5	$^6H_{5/2}$	4.2	8.0	7.0
Eu^{+++}	6	$^7F_0$	0	17.9	18.0
Gd^{+++}	7	$^8S_{7/2}$	39.4	40.0	40.2
Tb^{+++}	8	$^7F_6$	48.3	47.1	44.8
Dy^{+++}	9	$^6H_{15/2}$	52.8	52.2	53.0
Ho^{+++}	10	$^5I_8$	52.8	52.0	51.9
Er^{+++}	11	$^4I_{15/2}$	47.7	47.0	46.7
Tm^{+++}	12	$^3H_6$	37.6	35.6	37.5
Yb^{+++}	13	$2F_{7/2}$	22.5	21.9	22.5
Lu^{+++}	14	$^1S_0$	0	diamagnetic	diamagnetic

In general the agreement is good, and only in the case of Sm^{+++} and Eu^{+++} are there any serious disagrements.

Following the method of Laporte (27), Van Vleck and Frank (28) took the value of 34 for the screening constant of europium and by including the second-order Zeeman terms obtained a value for the apparent Bohr magneton number (at room temperature) of about 3.5. This is equivalent to about 17.5 Weiss magnetons and agrees well with the experimental values of Cabrera and St. Meyer (loc. cit.).

Freed, in 1930, measured the susceptibility of $Sm_2(SO_4)_3.8H_2O$ from 74° to 291° K. (29), and has shown that the samarium ion both in solids and in solutions consists of a mixture of electronic isomers, which appear to be in thermal equilibrium. The variation of the magnetic susceptibility suggests that the stable isomer at the lowest temperature has the configuration:

Sm^{+++} shell:	1 s (2s to 4d)	4f 5s 5 p
No. of electrons:	2 (full)	5 (full)

The configuration predicted by Hund (4f5, $^6H_{5/2}$) holds for low temperatures. At higher temperatures, however, due to the Boltzmann distribution factor, many of the atoms are in excited states whose energy values are but slightly greater than that of the $^6H_{5/2}$ term. A further prediction of Freed was that the relative intensities of the lines would vary with temperature, and such a variation was actually found in the case of $SmCl_3.6H_2O$ (30).

Amelia Frank, in extending the work of Van Vleck, made some interesting calculations on temperature dependence of the susceptibilities (31). If, for some salts, Curie's law does not hold, the Curie constant is not independent of temperature. Therefore previous work was in reality a comparison of susceptibilities at a given temperature. Deviations from Curie's law for neodymium in the straight line portion of the curve are expressed by the following relation:

$$\chi_m = \frac{C}{T+\Delta}$$

where the significance of Δ is as shown in Figure 1:

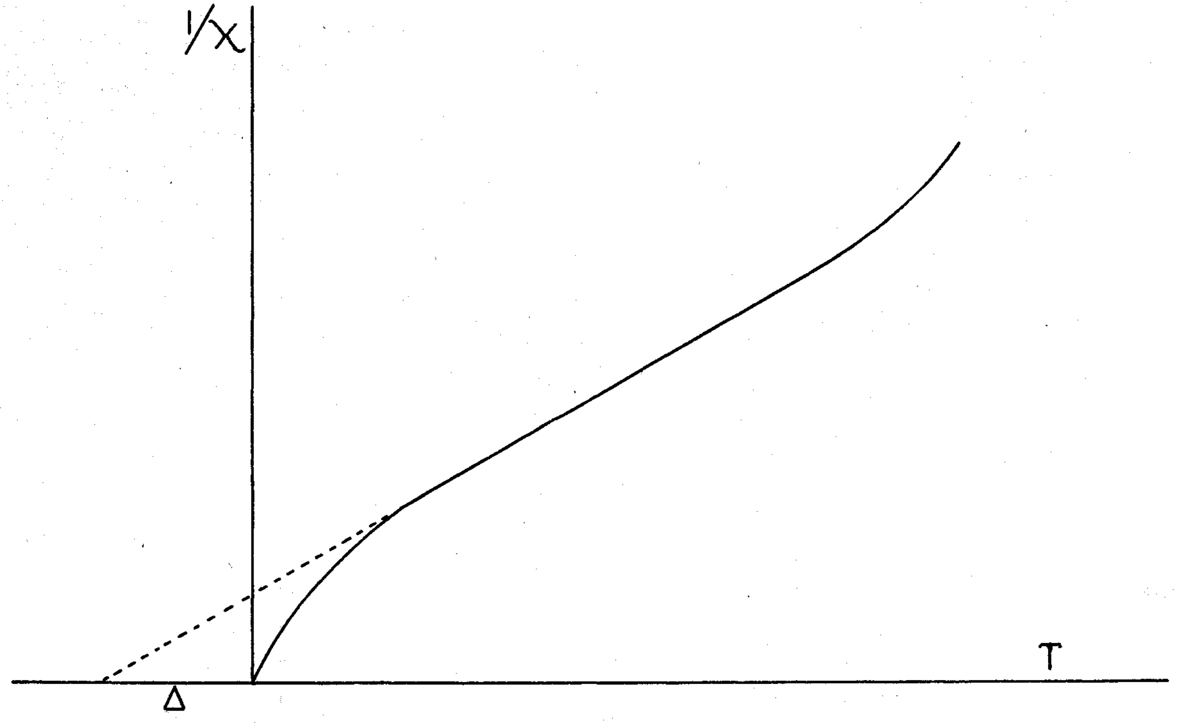

Fig. 1. Variation of magnetic susceptibility with temperature.

Penney and Schlapp, working on the influence of crystalline fields on the susceptibilities of salts of paramagnetic ions, have developed formulas for the calculation of susceptibilities directly from multiplet intervals (12). Excellent agreement is obtained with the experimental results of Gorter and de Haas for the variation of susceptibility with temperature if the assumption is made that the crystal field has cubic symmetry and can be represented by a potential D $(x^4 + y^4 + z^4)$. For the case of neodymium the following equation was developed:

$$\chi = (2g^2\beta^2N/A)\Big[(0.1483e^{19.59\mu} + 0.2396e^{-9.11\mu} - 0.3879e^{-20.95\mu})$$
$$+ \mu(6.065e^{19.59\mu} + 4.031e^{-9.11\mu} + 1.680e^{-20.95\mu})\Big]$$
$$\div \left[2e^{19.59\mu} + 2e^{-9.11\mu} + e^{-20.95\mu}\right]$$

where $g = 8/11$ for Nd, $\mu = A/kT$, β is the Bohr magneton and N is Avogadro's number. A is found by solving the energy level equations. This equation is very sensitive to the shape of the susceptibility curve versus temperature but is not sensitive to the absolute value of the susceptibility since the arbitrary parameter A in the equation is determined from the absolute value. If, on the other hand, the absolute values of Selwood (49), Zernicke and James (16) and Cabrera (26) are used a different value of A is obtained which is in agreement with A obtained from spectra.

Recent work of Cabrera (32) has shown that the discrepancies between the magnetic constants derived from the wave-theory of magnetism and those obtained by experiment are largely due to the presence of foreign materials, primarily water, in the substances used for the experimental work. The relevant facts may be concisely presented by the curves shown in Figure 2:

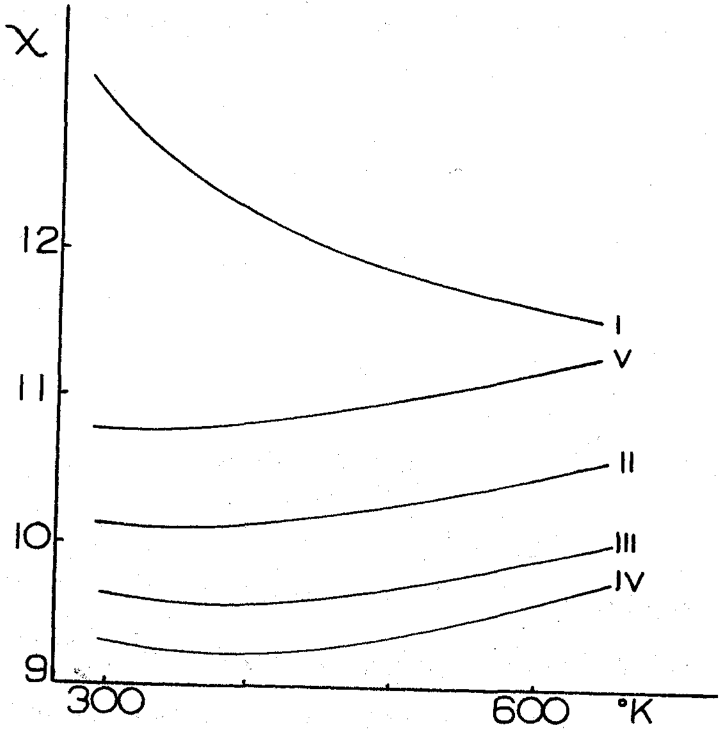

Fig. 2. Effect of water-occlusion on the variation of susceptibility with temperature.

Curve I = sample of Sm_2O_3 from Rolla

Curve II = sample of Sm_2O_3 from Prandtl (A)

Curve III = sample of Sm_2O_3 from Prandtl (B)

Curve IV = sample of Sm_2O_3 from Urbain

Curve I was found to be due to the presence of about 1% of gadolinium. When a correction was applied for this impurity, the curve coincided with III. Further, when curves II, III and IV were corrected for the water content of the sample concerned, they all took up the position shown by the curve V.

Therefore it can be easily seen that it is very important that pure materials be used, that analysis be made and reported and that methods of preparation of sample be accurately reported.

C. Specific Heat

Some very interesting work on the relationships of specific heat to electronic activation in rare earth crystals has been done, during the last few years by Ahlberg and co-workers at Berkeley and Johns Hopkins.

In a letter to the editor of Physical Review, Ahlberg and Freed (33) discussed the magnetic (34) and optical (35) behavior of the samarium ion in crystals. These properties show clearly that Sm^{+++} possesses an electronic level little removed in energy from its basic level and that a considerable change in the relative populations of the two states is occurring near the temperature of liquid nitrogen. The determination of the specific heat of Sm^{+++} as a function of temperature would then yield a check on the electronic transitions in a crystal as ascertained from the spectra.

An expression relating change in specific heat at constant volume with transitions between quantum states has been given by Schottky (36):

$$\Delta C_v = \frac{mR(h\nu/KT)^2 e^{\frac{h\nu}{KT}}}{(e^{\frac{h\nu}{KT}} - m)^2}$$

where <u>m</u> is the ratio of the statistical weights in the activated and in the basic state and <u>ν</u> is value of the energy difference between the basic and activated state.

The contribution to the specific heat due to translational, vibrational and crystal frequencies should be the same for samarium sulfate and gadolinium sulfate, since they have exactly the same crystal structure and the masses of the atoms can be taken as the same with very small error. Spectra (37) and magnetic susceptibility (38) data have established the fact that all the gadolinium ions occupy the basic electronic state $^8S_{7/2}$ from room temperature to the temperature of liquid hydrogen. Therefore measurements on the octahydrated gadolinium sulfate (39) could be used to give the specific heat of octahydrated samarium sulfate in the basic state. The net electronic specific heat of Sm^{+++} within small limits of error thus equals the difference between the heats for samarium sulfate and gadolinium sulfate.

Later work on the same salts by Ahlberg and associates over the temperature range 16° to 300° K. (40) made the statistical weights of all three excited levels as found spectroscopically by Spedding and Bear (41) the same, and equal to that of the basic state. The levels were 0, 160, 188 and 225 cm^{-1}.

Giaque in his paper on spectroscopic calculations (42) gives the following theoretical equation, a more complete form of the Schottky equation, for the calculation of the heat capacity due to the degrees of freedom considered:

$$C_{v(\mathrm{electronic})} = \frac{N}{KT^2}\left[\frac{\Sigma \varepsilon^2 p\, e^{-\varepsilon/KT}}{\Sigma\, p e^{-\varepsilon/KT}} - \left(\frac{\Sigma \varepsilon\, p\, e^{-\varepsilon/KT}}{\Sigma\, p e^{-\varepsilon/KT}}\right)^2\right]$$

where N is Avogadro's number, ε equals $h\nu c$ in which ν is the energy difference between states in reciprocal centimeters and p is the 'a priori' probability.

Using the data of Spedding and Bear (loc. cit.) and the theoretical equation for the electronic heat capacity, Amelia Frank (43) calculated the heat capacity of samarium at various temperatures and plotted the theoretical curves (Fig. 3). The lack of good agreement with the absolute values of Ahlberg and Freed (44) was not considered surprising. The experimental values were obtained by the above mentioned method and represent the differences between the heat capacities of $1/2\ [Sm_2(SO_4)_3.8H_2O]$ and $1/2\ [Gd_2(SO_4)_3.8H_2O]$. Since these are large quantities relative to their difference, the possible error in the difference may be considerable. However, Miss Frank has used only three of Spedding's levels in her calculations since simple theory only permits this number. The other levels she attributes to crystal vibrations. Ahlberg using all of the levels as reported by Spedding, and assigning to each a statistical weight of two, calculated a curve which fitted the experimental very closely. In using this method of calculation it must be borne in mind that the position of the peak of the curve gives a check of the levels, while the statistical weight determines the height.

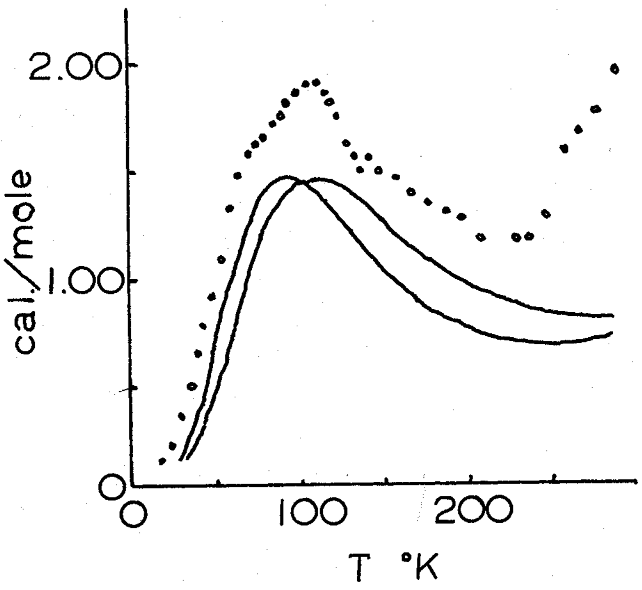

Fig. 3. Variation of electronic heat capacity of Sm^{+++} with temperature. Solid lines show theoretical values of Frank using levels at (a) 187 and 225 $cm.^{-1}$, (b) 160 and 187 cm^{-1}. Circles designate experimental values of Ahlberg and Freed.

When it became possible to extend the measurements to cover the range 3° to 40° K. (45), the neodymium sulfate octahydrate was included and gave an interesting check with spectroscopic data. The absorption spectra of the sulfate of neodymium were measured by Spedding, Hamlin and Nutting (46) and two excited levels were found at 77 cm.$^{-1}$ and 260 cm.$^{-1}$ from the basic state. The 260 cm.$^{-1}$ level does not enter the question because its population is negligible at temperatures below 40 K., but the heat capacity calculated from the 77 cm.$^{-1}$ level, using statistical weight for the level twice that of the basic level as predicted by theory, agrees closely with that found by direct experiment.

III. EXPERIMENTAL

A. Materials

The neodymium used in this research was a sample of hydrated neodymium magnesium double nitrate, $Nd_2Mg_3(NO_3)_{12} \cdot 24\ H_2O$, from the private laboratory of H. N. McCoy in Los Angeles, California.

In the present instance the neodymium was obtained as one of the by-products of the isolation of thorium oxide from monazite. The praseodymium and neodymium were separated by means of repeated fractional crystallizations of the magnesium double nitrates. In spite of the fact that extreme care was exercised and a large number of recrystallizations were performed in the preparation of this sample of neodymium, it still contained a small amount of praseodymium. This was evidenced by the definite appearance of the very strong absorption band of praseodymium in the 5900 A region of the spectra.

Preparations

(1) Neodymium bromate, $Nd(BrO_3)_3 \cdot 9H_2O$.

The neodymium magnesium nitrate was dissolved in cold conductivity water and the neodymium was then precipitated as the oxalate by adding a slight excess of a saturated solution of oxalic acid, according to the equation:

$$Nd_2Mg_3(NO_3)_{12} + 3(COOH)_2 = Nd_2 \quad (COO)_2 \quad _3 + 3Mg(NO_3)_2 + 6HNO_3.$$

At this point it might be mentioned that conductivity water was used throughout this investigation since the distilled water in the chemical laboratories was found to contain appreciable amounts of iron and dissolved carbon dioxide.

After digesting for a short time, on a hot plate at low heat, the precipitate was allowed to settle for an hour and then was recovered on "ashless" filter paper, dried, and ignited to constant weight in a large platinum dish.

$$Nd_2\ (COO)_2\ {}_3 = Nd_2O_3 + 3CO_2 + 3CO$$

The resulting neodymium oxide was a light blue powder. This was added to a large volume of cold water containing a slight excess of sulfuric acid required for the following reaction:

$$Nd_2O_3 + 3H_2SO_4 = Nd_2(SO_4)_3 + 3H_2O.$$

From the resulting clear solution the neodymium was again precipitated as the oxalate, filtered, dried and ignited to the oxide in order to obtain a very pure material to be used as the source of neodymium for subsequent preparations.

A weighed portion of the purified oxide was added to a large volume of water containing the theoretical amount of sulfuric acid for neutralization. Upon standing overnight a clear solution resulted.

To this solution of neodymium sulfate a solution of barium bromate was added which contained a slight excess of the barium salt as required by the equation:

$$Nd_2(SO_4)_3 + 3Ba(BrO_3)_2 = 2Nd(BrO_3)_3 + 3BaSO_4.$$

The resulting solution after digestion overnight at a temperature slightly below 100° C. was filtered to remove the precipitated barium sulfate.

The solution of neodymium bromate thus obtained was concentrated to the saturation point on a steam-bath. The first crystals to come out of solution were filtered out and discarded in order to remove any of the less soluble barium bromate which might have remained in solution.

A second batch of crystals was obtained by slow concentration of the mother liquor at room temperature by means of a vacuum desiccator containing fine mesh anyhdrous calcium chloride. A moderate vacuum was maintained in the desiccator by means of a water aspirator.

The crystals obtained from the vacuum evaporation were filtered out of the mother liquor into a sintered glass filtering crucible, washed and redissolved in cold water. This resulting solution was vacuum evaporated to obtain crystals of a high degree of purity.

This method gave large quantities of small well-formed crystals in a period of several days. However, to obtain large clear crystals suitable for single crystal measurements it was necessary to resort to a slightly different procedure. To a solution of the bromate which had started to crystallize a few drops of water were added and the resulting solution rapidly filtered, by means of vacuum, through a sintered glass crucible of medium porosity. A single well-formed crystal of the bromate was carefully placed in the filtrate and the resulting solution contained in a small beaker was set in a desiccator containing anhydrous calcium chloride. The desiccator was kept in the spectrograph room where the temperature remained practically constant in order to insure symmetrical growth of the crystal. By this procedure single crystals having the dimensions 15 mm. by 10 mm. by 4 mm. were obtained.

Since there was always the possibility that the salt obtained was not, as assumed, the nonahydrate, or even the trivalent bromate, an analysis of the salt was made to establish the exact nature of the compound used for the investigation.

(2) Quantitative analysis of the bromate.

(a) Determination of Nd. The method was to precipitate as oxalate, ignite to the oxide, and weigh.

Found: 20.840% ; 20.890%

Average - 20.865%

Theoretical: 20.904%

(b) Determination of BrO_3. The method used here was the microchemical determination in which potassium iodide and glacial acetic acid were added to a solution of the salt. The iodine liberated by the bromate ion was titrated with standard sodium thiosulfate.

Found: 55.575%; 55.534%

Average - 55.560%

Theoretical: 55.585%

Since the theoretical percentages referred to were calculated from the formula $Nd(BrO_3)_3 \cdot 9H_2O$, it follows that the material was, actually, the nonahydrated tribromate, and also was in a very good state of purity.

(3) Neodymium oxide, Nd_2O_3.

This salt was prepared from neodymium nitrate which in turn was prepared from the purified oxide in very much the same manner as the sulfate. The solution of neodymium nitrate was concentrated and crystallized using a procedure identical to that for obtaining small crystals of the bromate. Small recrystallized crystals of the nitrate were dehydrated at a very low heat in a platinum crucible followed by prolonged heating to a cherry-red heat at which time the nitrate decomposed to the oxide (25):

$$4Nd(NO_3)_3 = 2Nd_2O_3 + 12NO_2 + 3O_2$$

The oxide obtained in this manner was very light blue in color and retained its color following cooling.

Samples of the oxide prepared from the ignition of the oxalate were also used in the investigation as a check against the general procedure using the nitrates'

Neodymium oxide has been found to exist in two different crystalline modifications. These two types are prepared by ignition at different temperatures. Both types were prepared and their spectra photographed. The low temperature oxide's spectra contains more lines but since it is actually a mixture of types A and C instead of entirely type A, as is the high temperature oxide, its spectra is not of as much theoretical importance.

(4) Quantitative analysis of the oxide

The oxide was analyzed for its neodymium content by dissolving in dilute hydrochloric acid followed by precipitation as the oxalate as described in the case of the bromate.

Found: 85.568%; 85.933%

Average: - 85.755%

Theoretical: 85.738%

B. Apparatus

(1) Source of light

A 500 watt tungsten filament projection lamp housed in a metal box having a large condensing lens in one end was found satisfactory for all the ranges covered.

(2) Absorption cells

These varied with the type of sample in use, and also with the temperature range in which one wished to operate. Two primary types of samples were employed:

(a) Single crystals (1-6 mm. thick).

(b) Conglomerates (0.1-5 mm. thick).

In case (a), the crystal chosen was simply attached to a piece of cardboard with a suitable hole cut through which the light could be passed. This type of sample could be used at room temperature and at the temperature of liquid nitrogen.[1] In making room temperature exposures it was necessary to pass the light from the lamp house first through a large beaker full of water, in order to absorb the great heat carried by the rays.

In case (b), two methods were employed: (1) Salts obtained in moderate sized crystals were placed in small glass flasks having plane parallel sides. These flasks were made by blowing out tubing of suitable

---

[1] Liquid nitrogen was used in preference to liquid air since the oxygen in the latter gives wide absorption bands.

diameter into carbon moulding blocks. (2) In the case of the oxide it was impossible to make glass cells with parallel sides thin enough. Therefore, a thin layer of the material was placed between two pieces of glass which were held together by adhesive tape. The whole affair was then fastened to a piece of cardboard in much the same manner as a single crystal would be mounted.

(3) Cooling jackets

Liquid nitrogen, boiling at -195.8° C., and liquid ethylene, boiling at -103.9° C., were used for the production of low temperatures. The liquids were contained in a large Dewar flask, in which the samples were supported by long wooden dowel sticks. The Dewar was similar to those described by Spedding and Bear (48), the light passing through the flask by means of two triangular windows left in the silvering of the sides.

This Dewar flask had an internal diameter of 4.5 inches and a depth of about 2.5 feet. By having such a large jacket, it was possible to make a long exposure, or several shorter ones, without the necessity of refilling with liquid nitrogen.

For the carbon dioxide in acetone temperatures (-78.5° C.) an unsilvered Dewar flask of one liter capacity was used.

(4) Cooling mediums

The solid carbon dioxide was the ordinary commercial grade.

The liquid nitrogen was obtained from the Air Reduction Sales Company and was of a purity greater than 95 percent.

Liquid ethylene was prepared as needed by allowing ethylene, in the gas form, to flow into a brass pipe which was surrounded by liquid nitrogen, the condensed gas flowed through the pipe into the large Dewar flask previously described. As the ethylene vaporized it was recondensed and returned to the bottom of the flask.

(5) Reference spectrum

This was obtained, superimposed upon the absorption spectrum, by replacing the cell containing the sample with an iron arc using a direct current of from 3 to 5 amperes across a gap of 5 to 7 mm.

(6) Recording instruments

In this investigation three different instruments were used:

(a) A Hilger El Littrow type quartz spectrograph, giving a dispersion of 36A. per mm. in the 6300 A. region, and 7 A. per mm. in the 3500 A. region.

(b) A three meter grating spectrograph using a grating ruled by Wood having 14,448 lines per inch and mounted in a modified Wadsworth mounting which gave a linear dispersion of about 11 A. per mm.

(c) A 21 foot grating spectrograph using a grating also having 14,448 lines per inch but in this instance utilizing the Paschen mounting which gave a linear dispersion of about 2.5 A. per mm. in the first order.

(7) Photographic plates

All plates used were manufactured by Eastman Kodak and were of the following types:

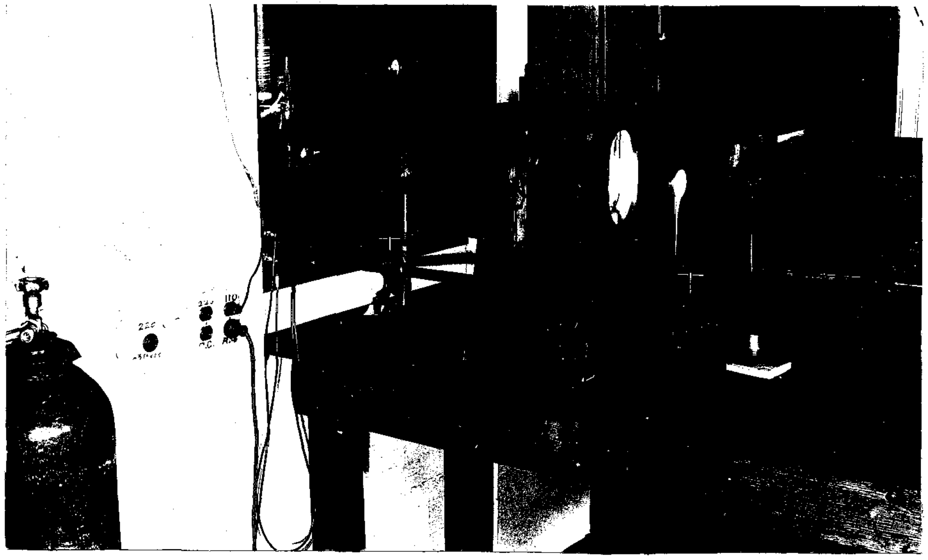

Fig. 4. Optical line-up for the twenty-one foot grating spectrograph.

(a) From 8500 A. to 7500 A., 144-R.

(b) From 8000 A. to 6500 A., 1-N.

(c) From 7000 A. to 5000 A., I-S, 103-F.

(d) From 6500 A. to 4000 A., Super Panchro Press., 103-B.

(e) From 5000 A. to 3800 A., I-O, 103-O, Ia-O.

(8) Measuring engine

This was a comparator manufactured by the Societe Genevoise of Geneva, Switzerland. It had a 2 mm. pitch screw and gave readings to 0.001 mm.

C. Method of Procedure

(1) Exposures

For each salt, plates were taken with conglomerates and single crystals, except in the case of the oxide where only thin conglomerates were used. In order to obtain the best exposure for every absorption line observed, the same region had to be photographed a number of times, since an exposure giving good results in one range would either over-expose the lines in the next range or fail to record them, owing to the variation of the intensity of the source and the sensitivity and type of the plates in the different regions of the spectrum.

In the visible, exposure times varied from five minutes to forty-eight hours, while in the near infra-red exposures of two to forty-eight hours were made. Exposure times also varied inversely as the dispersion of the instrument.

The final result was a set of plates which included at least two independent recordings of every neodymium line observed at both room temperature and liquid nitrogen temperature for each of the types of sample employable for the salt under consideration. For intermediate temperatures one complete set of conglomerate plates only was obtained. In the case of the polarized spectra, one complete set of plates for each of two different thin crystals and one set for a thick crystal were made.

The polarized spectra were obtained by placing a Wollaston prism in front of spectrograph slit. It was possible to so line up the prism that the parallel and perpendicular spectra fell one above the other on the slit and were thus recorded side by side for easy comparison (Fig. 5). The absolute intensity between the two spectra can not be relied on, since their intensity depends on the line-up of the prism and polarizibility of the instrument.

(2) Examination of plates

Before attempting to measure the exact position of any of the absorption lines, the plates were placed in turn on a ground-glass viewing box and carefully examined with a low-power jeweler's lens.

At this stage the degree of sharpness or diffuseness of the lines, and also the relative intensities could be noted. Also at this point certain very faint lines which, though clearly visible on the viewing box or with the jeweler's lens, were completely invisible through the high-power microscope of the comparator, could be marked by making a faint dot in the

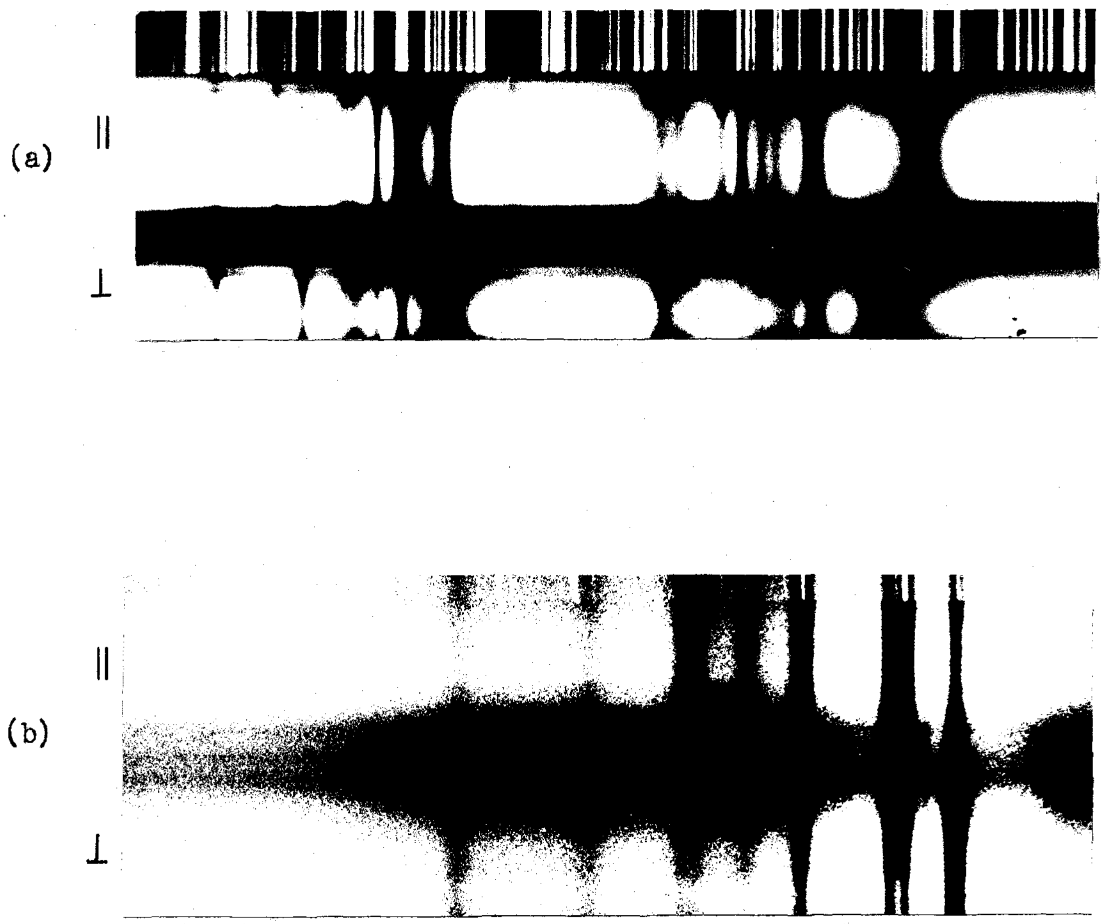

Fig. 5. Polarization spectra of a single crystal of neodymium bromate at liquid nitrogen temperature. (a) 5200A multiplet. (b) 6300 A multiplet.

gelatine with a sharp needle-like instrument. Such a mark as this could be readily observed and its position accurately measured.

(3) Measurements

It was found advantageous to measure only one multiplet of neodymium lines at a time. A plate having been clamped on the stage of the comparator in such a manner that no "hypotemuse effect" was observed in traversing from one end to the other, measurement was started with a characteristic and readily identified iron line and continued through the multiplet to end with another good iron line. Where possible, an iron line was measured in the immediate vicinity of every neodymium line. The measurement of each line was repeated several times and the mean recorded. In addition, the neodymium lines were measured on each side. Every line observed was measured on at least two different plates.

(4) Calculations

The manner in which the final wave numbers were obtained from the comparator readings may be best explained by taking a typical multiplet as an example:

$Nd(BrO_3)_3.9H_2O$, Grating plate #107, 6300-6200 A. In order to prevent corrections from becoming large, a separate extrapolation was made for every two hundred to three hundred Angstroms measured on the plate.

First, the initial and final iron lines were identified on the standard wave length chart put out by Hilger of London. These two wave lengths were recorded in the third column of Table II . Assuming a linear relation between wave lengths and millimeters, the figures in the fourth column were obtained on a ten bank electric calculator.

From the extrapolated wave length, each iron line could be identified either on the Hilger charts or in Kayser and Konen: "Handbuch der Spectroscopie", and the correct wave length read off and recorded in column three.

By subtracting the extrapolated wave lengths of the iron lines from the accurate values in the third column, the corrections in column five were obtained.

The next step was to graph the millimeters of the iron lines against the corrections in wave length units. This should give a smooth curve with its peak at the mid-point of the extrapolation. If such was not the case, one of the "anchor" lines was probably wrongly identified, and the extrapolation had to be repeated using another iron line.

Next, the corrections which applied to the extrapolated wave lengths of the neodymium lines were read off from the curve and added to the values in column four to give the values in column six.

Finally, the wave number values recorded in column seven were obtained by the use of Kayser's conversion tables applied to the values in column six which also corrected to represent measurements in a vacuum.

(5) Enlargements and prints

Contact prints were made from the grating plates. In doing this, it was found that in some cases only a portion of a plate could be properly printed with a given exposure time. Complete spectrograms covering the range from 8500 A. to 3800 A. were made by cutting various exposures from

Table II. Specimen calculation for one multiplet

Line	mm.	A_{Fe}	A_{Ex}	Diff.	$A_{Corr.}$	Cm.$^{-1}$
Fe	151.078	6301.52				
Fe	152.640	6297.803	6297.79	+.01		
Nd	159.744		6280.82		6280.9	15916.9
	160.890		6278.08		6278.1	15924.0
Nd	161.496		6276.63		6276.7	15927.5
	162.796		6273.52		6273.6	15935.4
Nd	165.796		6266.36		6266.4	15953.7
	166.676		6264.25		6264.3	15959.1
Fe	166.311	6265.145	6265.11	+.04		
Fe	169.995	6256.371	6256.32	+.05		
Fe	170.866	6254.266	6254.22	+.05		
Nd	170.560		6254.97		6255.0	15982.8
	171.030		6253.85		6253.9	15985.6
Nd	171.420		6252.92		6253.0	15987.9
	171.770		6252.08		6252.1	15990.2
Fe	171.585	6252.567	6252.52	+.05		
Fe	174.185	6246.344	6246.31	+.03		
Nd	179.120		6234.52		6234.5	16035.4
	179.630		6233.30		6233.3	16038.4
Fe	179.900	6232.667	6232.65	+.02		
N Nd	180.620		6230.93		6231.0	16044.4
	181.000		6230.03		6230.1	16046.7
Fe	180.719	6230.734	6230.71	+.02		
Nd	185.000		6220.47		6220.5	16071.4
	185.410		6219.49		6219.5	16074.0
Fe	185.493	6219.290				

different plates at suitable points and joining together in the correct position. This was done for the various temperatures and the complete spectrograms were mounted side by side.

These prints gave a ready means of examining the various spectra in their entirety and of comparing the one with the other.

In the case of the plates from the prism instrument enlarged prints were made to facilitate examination of the spectra.

(6) Chart of lines

To simplify the interpretation of the results and the search for recurring frequency intervals, a plot was made of the positions of all the absorption lines as measured in wave number units. This was done on a sheet of graph paper measuring 1 1/2 by 8 feet. The sheet was divided into ten major strips lengthwise, and each 5 cm. in depth. These strips were graduated consecutively allowing a 300 cm.$^{-1}$ overlap on a scale of one wave number unit per mm., giving a range from 11,000 cm.$^{-1}$ to 30,000 cm.$^{-1}$. The absorption lines were represented by a horizontal line whose length corresponded to the width of the absorbed line. The various temperature measurements were distinguished from one another by the use of different colored lines.

In the first plot, all measurements made were put down, and from these the weighted-mean values given in the following tables were taken.

Finally, a second plot was made giving only the mean values for the various temperatures. On this chart the values for the several salts were recorded so the effect of a change of a negative group could also be studied.

This final chart was used to make deductions from the results which will be discussed later.

IV. RESULTS

In the tables of results now presented primed lines in the single crystal, nitrogen temperature column of the bromate were obtained from polarized plates, while all lines reported for the oxide were obtained from thin layers of the powdered oxide. The letter "H" denotes a line which is markedly intensified at high temperatures and may not be picked up at all at low temperatures. Likewise, "L" denotes a line for which we have good evidence that it originates from the lowest or basic state and is electronic in origin. These letters are given in a separate column headed "T". The columns headed "I" give the intensities of the lines as estimated visually with respect to other neighboring lines on a scale from 0 to 10. A line marked 0 was so faint it was barely visible on the plate to the naked eye, while a line marked 1 was barely discernible under a low power eye-piece. These lines were measured by scratching the gelatine of the plate as previously described. A line makked 5 appeared completely absorbed in the conglomerate but not in the single crystal, while 10 denotes a line completely absorbed in both. These intensities are only relative to each other in the same spectral region and can not be compared with lines in different regions or in other spectra. The letter "s" signifies that the edges of the line or band were clear and sharp; "d" that the edges were not clearly defined; "vd" lines regardless of intensity had to be scratched in order to locate the edges due to gradual fading or extreme diffuseness; and "?" that the line was only observed on one plate.

In the columns marked "p" of the bromate are given the descriptive intensities of the single crystal lines as they appear in polarized spectra. The first of the two values is for perpendicular polarization, the second for parallel.

Table III. Absorption lines of $Nd(BrO_3)_3 \cdot 9H_2O$

Liquid N_2 temp.							Room temp.					
conglomerate				single crystal			conglomerate				crystal	
A	cm.$^{-1}$	I	T	cm.$^{-1}$	I	P	A	cm.$^{-1}$	I	T	cm.$^{-1}$	I
							8593.2	11634				
8591.8	11636											
8588.7	11640	10s										
							8586.5	11643	5d			
8549.9	11693						8550.6	11692				
8546.1	11698	10d			10s	7s						
							8543.4	11702	10d			
8525.6	11726						8525.2	11727				
8514.5	11741	4d					8514.8	11741	2vd			
8507.8	11751						8508.2	11750				
8497.1	11765	4d					8497.4	11765	2vd			
							8485.7	11781				
8479.5	11790											
							8476.5	11794	1vd			
8471.8	11801	1vd										
							8470.0	11803				
8466.9	11807											
8458.4	11819	1vd					8458.2	11820	2vd			
8447.1	11835											
8444.3	11839	3d										
							8442.7	11841				
8441.0	11844											
8438.1	11848	3d										
8436.9	11849											
							8433.3	11854	4vd			
8432.4	11856	7d										
8427.5	11863											
8422.6	11870	2vd										

Table III. (Continued)

Liquid N_2 temp.							Room temp.					
	conglomerate			single crystal				conglomerate			crystal	
A	cm.$^{-1}$	I	T	cm.$^{-1}$	I	P	A	cm.$^{-1}$	I	T	cm.$^{-1}$	I
							8418.9	11875				
8417.7	11876											
8413.1	11883	2vd										
							8408.4	11890	5vd			
8404.9	11895											
							8403.5	11897				
8398.9	11903	7d										
							8394.3	11910	5vd			
8392.7	11912											
8388.7	11918	4d										
							8381.8	11927				
8380.2	11930											
8375.0	11937	5d										
							8373.9	11939	3vd			
							8362.5	11955				
8361.3	11957											
8357.6	11962	8d										
8351.3	11971						8351.1	11971	8d			
8347.5	11976	8d										
8339.3	11988											
8335.7	11993	5d										
							8192.7	12203				
8188.9	12208											
							8151.6	12264	2vd			
8151.0	12265	2vd										
8146.2	12272											
8143.2	12277	4s										

Table III. (Continued)

	Liquid N_2 temp.						Room temp.					
	conglomerate			single crystal				conglomerate			crystal	
A	cm.-1	I	T	cm.-1	I	P	A	cm.-1	I	T	cm.-1	I
8071.9	12385											
8067.6	12392	7d										
8055.5	12410											
8051.1	12417	8d				5d 0d						
							8050.5	12418				
8047.6	12423											
8044.4	12428	8d				8d 1d						
							8042.5	12431	8d			
8039.3	12435											
							8038.7	12436				
8034.7	12443	10d										
							8031.6	12447	8d			
8027.4	12454											
8023.4	12460	9d										
8012.5	12477						8012.4	12477				
8010.5				12480'								
8006.8				12486'		8d 10d						
7999.0				12498'								
7994.2				12506'		10d 10d						
7990.9				12511'								
7986.1				12518'		10d 7d						
7979.6	12528	7vd					7979.8	12528	3vd			
7952.6	12571											
7950.4	12575	7s										
							7948.7	12577				
7946.9	12580											
7940.7				12590'								
7924.0				12616'		10d 10d						
7908.0	12642	7vd					7915.6	12630	8vd			

Table III.(Continued)

Liquid N_2 temp.							Room temp.					
	conglomerate			single crystal				conglomerate			crystal	
A	cm.$^{-1}$	I	T	cm.$^{-1}$	I	P	A	cm.$^{-1}$	I	T	cm.$^{-1}$	I
							7846.2	12742				
7845.6	12742											
7843.6				12746'								
7837.0				12756'		4d 10d						
							7830.7	12767	8vd			
7929.6	12769	7vd										
							7812.0	12797				
7810.6	12800											
7808.9				12802'								
7804.7				12809'		2d 8d						
7803.5	12811	8d										
							7802.3	12813	6d			
							7796.3	12823				
7793.4	12828											
7788.6	12836	8d				1s 3s						
							7787.5	12838	3d			
7779.2	12851											
7772.9	12862	1vd										
7763.3	12878											
7757.2	12888	1vd					7756.9	12888				
7746.7	12905											
7738.3	12919	3vd										
7735.3	12924											
7725.6	12940	3vd										
7722.1	12946											
7713.6	12961	3vd										
7710.4	12966											
							7709.3	12968	1vd			
7703.9	12977	2vd										

Table III. (Continued)

	Liquid N_2 temp.							Room temp.				
	conglomerate			single crystal				conglomerate			crystal	
A	cm.$^{-1}$	I	T	cm.$^{-1}$	I	P	A	cm.$^{-1}$	I	T	cm.$^{-1}$	I
7695.9	12990											
7688.2	13003	2vd										
7674.5	13027											
7658.8	13052	1vd										
7644.7	13077											
7634.3	13095	2vd										
							7630.3	13102				
7628.5	13105											
7623.8	13113	6d										
							7619.1	13121	5d			
							7609.8	13137				
7608.8	13139											
7606.4	13143	8s										
							7604.6	13146	9s			
7593.9	13165						7593.8	13165				
7591.6	13169	6s										
							7587.7	13176	5d			
7585.7	13179											
							7585.0	13180				
7582.2	13185	4vd										
							7578.8	13191	2vd			
							7557.9	13228				
7547.8	13245											
7542.9	13254	1vd										
							7539.9	13259	5vd			
7526.7	13282											
							7523.6	13288				
7520.7	13293	5vd										
							7517.0	13300	8vd			

Table III. (Continued)

Liquid N_2 temp.							Room temp.					
	conglomerate			single crystal				conglomerate			crystal	
A	cm.$^{-1}$	I	T	cm.$^{-1}$	I	P	A	cm.$^{-1}$	I	T	cm.$^{-1}$	I
							7514.1	13305				
7513.3	13306											
7512.7				13307'								
7508.3				13315'		6d 2 d						
7506.8	13318	9d										
							7500.8	13328	8vd	H		
7473.3	13377			13377'								
7470.0				13383'		6d 2d						
7468.7	13385	8d										
							7466.2	13390				
7451.6	13416											
7449.5				13420'								
7439.8				13438'		1d 10d						
7438.4	13440	9vd	HL									
7420.8	13472											
7416.5				13480'								
7411.2				13489'		10d 1d						
7406.2				13498'								
7403.4	13504	10vd	H									
7402.8				13505'		10d 10s	7402.9	13505	10vd	H		
							7390.1	13528				
7386.8	13534											
7384.8				13538'								
7378.7				13549'		10d 10s						
7373.4	13560	10vd	L									
							7372.2	13561	10vd			

Table III. (Continued)

Liquid N_2 temp.							Room temp.					
	conglomerate			single crystal				conglomerate			crystal	
A	cm.-1	I	T	cm.-1	I	P	A	cm.-1	I	T	cm.-1	I
							7356.2	13590				
7354.6	13593			13593'								
7340.5	13619	10vd	L	13619'		3d 10d						
							7335.7	13628	10vd			
							7317.3	13662				
7315.1	13666											
7313.6				13669'								
7312.6				13671'		10s 10d						
7311.6				13673'								
7310.4				13675'		10s 10d						
7308.4	13679	10d										
							7304.1	13687	10d			
7283.1	13727											
							7280.3	13732				
7277.0	13738	4vd										
7272.5	13747											
7265.6	13760	4vd										
							7264.9	13761	1vd	H		
7262.3	13766											
							7255.3	13779				
7254.5	13781	4vd										
7247.8	13794											
7240.0	13808	7vd										
							7239.2	13810	1vd	H		
7231.7	13824											
7228.4	13831	4vd										
7226.8	13834											
7219.4	13848	4vd										

Table III. (Continued)

	Liquid N_2 temp.						Room temp.					
	conglomerate			single crystal				conglomerate			crystal	
A	cm.$^{-1}$	I	T	cm.$^{-1}$	I	P	A	cm.$^{-1}$	I	T	cm.$^{-1}$	I
7211.7	13863											
							7208.3	13869				
7202.8	13880	4vd	L									
7198.4	13888											
7191.7	13901	6vd	L									
							7190.4	13904	1vd			
7182.5	13919											
7177.2	13929	4vd										
7164.1	13955											
7158.5	13966	3vd										
7155.1	13972											
7145.8	13990	3vd										
7130.0	14021											
7124.0	14033	4vd										
7111.6	14058											
7104.7	14071	1vd										
							6910.9	14466				
							6903.7	14481	8vd	H		
							6891.3	14507				
							6883.3	14524	6vd	H		
6831.5				14634								
6831.0	14635											
6827.8	14642	5d		14642	5d	3d 0d						

Table III. (Continued)

Liquid N_2 temp.							Room temp.					
	conglomerate			single crystal				conglomerate			crystal	
A	cm.-1	I	T	cm.-1	I	P	A	cm.-1	I	T	cm.-1	I
6823.1	14652						6822.7	14653				
6822.2				14654								
6818.0	14663	5d										
6817.1				14665	5d	3d 1d						
							6814.7	14670	6vd	H		
6798.5	14705			14705			6797.6	14707				
6794.8	14713	10d		14713	9d	3s 8s						
6790.7	14722			14722								
6787.0	14730	10d		14730	10d	10d 5d	6785.6	14733	10vd	H		
6782.8	14739			14739								
6781.0	14743	9d		14743	8d	2d 4d						
6766.8	14774			14774			6769.5	14768				
6763.1	14782	7d	L	14782	7d	8d 2d	6762.7	14783	4vd	H		
6745.3	14821			14821								
6742.6	14827	6s	L	14827	6s	1d 2d						
6738.0	14837			14837								
6736.7	14840	6d	L	14840	6d							
6735.3	14843			14843			6734.0	14846				
6733.5	14847	6d	L	14847	6d							
6731.7	14851			14851								
6728.1	14859	10d	L	14859	10d	10s 10s	6729.4	14856	6d	L		
6714.5	14889			14889			6714.5	14889				
6710.9	14897	10d	L	14897	10d	5s 10s						
							6709.1	14901	6d	L		

Table III. (Continued)

	Liquid N_2 temp.							Room temp.					
	conglomerate			single crystal					conglomerate			crystal	
A	cm.$^{-1}$	I	T	cm.$^{-1}$	I	P		A	cm.$^{-1}$	I	T	cm.$^{-1}$	I
								6408.1	15601				
								6397.0	15628	1vd	H		
								6386.8	15653				
								6367.8	15700	4vd	H		
6328.2	15798			15798									
6326.2	15803	6d	H	15803	4d								
								6325.0	15806				
								6317.4	15825	3vd	H		
6299.9	15869			15869									
6297.9	15874	4d	H	15874	3d			6298.7	15872				
								6292.3	15888	2vd	H		
6280.5	15918			15918				6283.2	15911				
6278.1	15924	7d	H	15924	5d	4d	7d						
6276.5	15928			15928									
6274.5	15933	7d	H	15933	5d	4d	7d	6274.5	15933	3vd	H		
								6269.0	15947				
6266.7	15953			15953									
6263.9	15960	7d	H	15960	4d	4d	7d						
								6262.8	15963	2vd	H		
								6256.6	15979				
6254.5	15984			15984									
6253.7	15986	8s	L	15986	8s	3s	10s						
6253.0	15988			15988									
6251.8	15991	10s	L	15991	10s	5s	10s						
								6248.7	15999	6d	L		
6234.6	16035			16035				6234.6	16035				
6233.1	16039	10s	L	16039	10s	10s	10d						
6231.1	16044			16044									
6230.0	16047	10s	L	16047	10s	10s	10d	6230.0	16047	8d	L		

Table III.(Continued)

	Liquid N_2 temp.						Room temp.					
	conglomerate			single crystal				conglomerate			crystal	
A	cm.$^{-1}$	I	T	cm.$^{-1}$	I	P	A	cm.$^{-1}$	I	T	cm.$^{-1}$	I
6226.9	16055			16055								
6225.7	16058	4s		16058	4s	3s 4s						
6221.1	16070			16070			6221.4	16069				
6218.7	16076	10d	L	16076	9d	10d 8d						
							6218.0	16078	7d	L		
5332.7	18747			18747								
							5330.7	18754			18754	
5329.6	18758	2vd		18758	1vd							
5324.5	18776			18776								
5322.2	18784	2vd		18784	1vd	2d 1d						
							5320.8	18789	5vd	H	18789	1vd
5310.6	18825			18825			5310.6				18825	0
							5310.3	18826				
5308.1	18834	2vd		18834	1vd							
5304.7	18846											
5303.0	18852	1vd										
							5301.6	18857	5vd	H		
5297.4	18872											
5294.6	18882	?										
5291.5	18893			18893								
5288.7	18903	1vd	H	18903	1vd	2d 1d						
5283.3				18923								
5282.0				18927	1vd							
5278.4	18940			18940								
							5277.0	18945			18945	
5273.6	18957	10vd	L	18957	10vd	5d 2d						
							5270.0	18970	8vd		18970	5vd

Table III. (Continued)

	Liquid N_2 temp.							Room temp.				
	conglomerate			single crystal				conglomerate			crystal	
A	cm.$^{-1}$	I	T	cm.$^{-1}$	I	P	A	cm.$^{-1}$	I	T	cm.$^{-1}$	I
5268.6	18975			18975								
5266.1	18984	1vd	H	18984	1vd							
5258.4	19012			19012								
							5256.7	19018				
5255.3	19023	10d	L	19023	8d	0 3d	5255.6				19022	
							5252.6				19033	1vd
5250.4	19041			19041			5250.9				19039	
							5246.8				19054	3vd
5246.2	19056	10vd		19056	8vd	9d 1d	5246.2	19056	7vd	HL		
5238.3	19085						5239.1	19082				
5235.8				19094			5236.2				19093	
5234.2				19100	8d	1d 3d						
5232.8				19105								
5231.1	19111	10vd	L									
5230.6				19113	8d	3d 1d						
5229.8	19116						5229.8				19116	8vd
5225.7				19131								
5224.3				19136	10s	5s 10s						
5223.3	19140	10vd	L									
5220.2	19151											
5218.3				19158			5218.6				19157	
5215.6			L	19168	10d	10s 10d						
5213.2				19177'								
5210.7				19186'		0 7d						

Table III. (Continued)

	Liquid N2 temp.							Room temp.				
	conglomerate			single crystal				conglomerate			crystal	
A	cm.-1	I	T	cm.-1	I	P	A	cm.-1	I	T	cm.	I
5210.1				19188								
5200.7				19223	10vd	10d 10s						
							5199.6				19227	10vd
5192.6	19253	10vd					5199.0	19229	10vd			
5183.1	19288											
5182.6				19290								
5181.3				19295	7d	0 2d						
5179.1	19303	7vd										
5141.0	19446			19446								
							5140.2				19449	
5139.2				19453	6d	0 4s	5139.7	19451				
5137.1				19461			5137.6				19459	1vd
							5134.9				19469	
5133.4				19475	9d	8d 6s						
5129.9				19488								
5128.4				19494	7d	3d 5d						
5127.6	19497	10vd										
							5126.3				19502	8vd
5118.9	19530						5126.0	19503	10vd	H		
5116.8				19538			5117.3				19536	
5115.5				19543	8d	1d 7d						
5115.0	19545	10d										
							5112.9				19553	0d
5111.3	19559											
5110.8				19561								
5109.2				19567	9d	3d 10s						
5107.7	19573	10d										

Table III. (Continued)

	Liquid N_2 temp.							Room temp.					
	conglomerate			single crystal					conglomerate			crystal	
A	cm.$^{-1}$	I	T	cm.$^{-1}$	I	P		A	cm.$^{-1}$	I	T	cm.$^{-1}$	I
5104.8	19584			19584									
5103.0				19591	8d	2d	7s						
5101.7	19596	10d											
5099.8	19603			19603									
5098.5				19608	8d	3d	7s						
5090.0				19641				5089.5	19643			19643	
5083.2				19667	10vd	8d	10d	5083.5	19666	8d		19666	5d
5072.2				19710									
5067.8				19727	8vd	8d	4d						
5062.9				19746'									
5060.4				19756'		9d	3d	5058.6				19763	
								5057.3	19768				
5057.2				19768'				5049.1				19800	1vd
5048.3				19803'	10vd	7d	9d	5046.8	19809	3vd			
5041.2	19831	10vd											
								5038.7	19841	3vd			
5011.4	19949												
5001.9				19987									
4998.1	20002	5vd		20002	1vd								
4987.6	20044												
4971.0	20111	1vd											
4873.8	20512												
4867.9	20537	1vd											
4858.9	20575												
4852.8	20601	1vd											
4848.8	20618												
4838.2	20663	1vd											
4332.1				20689									
4830.3				20697	?								

Table III. (Continued)

	Liquid N_2 temp.							Room temp.					
	conglomerate			single crystal					conglomerate			crystal	
A	cm.$^{-1}$	I	T	cm.$^{-1}$	I	P		A	cm.$^{-1}$	I	T	cm.$^{-1}$	I
4829.8	20699												
4829.6				20700									
4827.5				20709	2vd								
4827.0	20711	3d											
4827.2	20713							4825.4	20718				
4824.0				20724									
4823.5				20726	10s	10s	1s						
4823.0	20728	10s											
4819.6	20743							4818.9	20746	1vd			
								4810.3	20783			20783	
4805.9	20802	1vd											
								4805.0				20806	2vd
								4803.4	20813	6vd	H		
								4779.5	20917				
4769.0				20963									
4768.5	20965												
4766.3				20975	6d	3d	4d	4766.0				20976	
4765.8	20977	8d											
4765.1				20980									
4764.7	20982												
4762.8				20990	6d	3d	4d						
4762.6	20991	8d											
4760.3	21001							4760.8				20999	4vd
4759.9				21003									
4758.5				21009	4d	2d	3d	4758.8	21008	8vd			
4758.3	21010	7d											

Table III. (Continued)

	Liquid N_2 temp.								Room temp.				
	conglomerate			single crystal					conglomerate			crystal	
A	cm.$^{-1}$	I	T	cm.$^{-1}$	I	P		A	cm.$^{-1}$	I	T	cm.$^{-1}$	I
4753.3				21032									
4753.1	21033							4753.1				21033	
								4752.9	21034				
4751.3				21041	8d	5d	3d						
4750.6	21044	10d											
4749.3	21050												
4749.0				21051				4748.6				21053	4vd
4747.0	21060	10d		21060	8d	2d	5d						
4744.8	21070			21070				4744.8	21070	8vd			
4742.5	21080	9d		21080	7d	0	3d						
4727.0	21149												
4726.8				21150									
4725.9				21154	9s	0	4s	4726.1	21153				
4725.7	21155	10s											
4725.3	21157												
4725.0				21158									
4724.4				21161	9s	0	6s						
4723.9	21163	10s											
4723.2				21166									
4723.0	21167							4722.6	21169	5d			
4722.3				21170	10s	5s	8s						
4721.5	21174	10d	L										
								4719.2	21184				
4718.6	21187			21187									
4717.7	21191	10s	L										
4717.2				21193	9s	1s	6s						

Table III. (Continued)

	Liquid N_2 temp.							Room temp.				
	conglomerate			single crystal				conglomerate			crystal	
A	cm.$^{-1}$	I	T	cm.$^{-1}$	I	P	A	cm.$^{-1}$	I	T	cm.$^{-1}$	I
4715.9	21199						4714.8	21204	5d			
4713.9	21208	2vd										
4702.4	21260											
4699.3	21274	2vd										
4686.5	21332											
4683.2	21347	4vd										
4681.2	21356											
4679.7	21363	?										
4674.7	21386											
4671.8	21399	?										
4660.1	21453											
4657.4				21465	0d							
4656.8	21468	1vd										
4652.9	21486			21486								
4650.7	21496	1vd										
4648.8				21505	1vd							
4646.8	21514											
4643.8	21528	1vd										
4641.2	21540											
4640.8				21542			4640.8	21542				
4639.5				21548	10d	5d 9s						
4638.9	21551	10d										
4634.8	21570											
4633.9				21574								
4633.1				21578	9d	3d 8s						
4632.2	21582	10d					4632.2	21582	3vd			

Table III. (Continued)

	Liquid N_2 temp.							Room temp.				
	conglomerate			single crystal				conglomerate			crystal	
A	cm.$^{-1}$	I	T	cm.$^{-1}$	I	P	A	cm.$^{-1}$	I	T	cm.$^{-1}$	I
4623.8	21621											
4623.6				21622								
4619.1	21643	5vd										
4618.3				21647	2vd	2d o						
4616.2	21657											
4615.1				21662								
4611.9				21677	7vd							
4611.3	21680	7vd				8d 5d						
							4610.0	21686			21686	
4607.0	21700											
4606.6				21702								
4601.9				21724	8vd	10d 5d						
4598.7				21739								
4595.1				21756	8vd	8d 5d						
4594.9	21757	10vd										
							4593.9	21762	6vd			
							4593.2				21765	3vd
4588.0	21790											
4680.2	21827	1vd										
							4537.0	22035				
4535.9				22040								
4534.9	22045	0vd					4534.7	22046	?			
							4532.4	22057				
							4527.5	22081	1vd			
4526.9				22084	1vd							

Table III. (Continued)

	Liquid N_2 temp.						Room temp.					
	conglomerate			single crystal				conglomerate			crystal	
A	cm.$^{-1}$	I	T	cm.$^{-1}$	I	P	A	cm.$^{-1}$	I	T	cm.$^{-1}$	I
							4523.8	22099				
4523.2	22102											
4522.4				22106								
							4517.9	22128	0vd			
4515.4				22140	1vd							
4514.8	22143	1vd										
4417.5	22631	?										
4347.0				22998								
4345.9	23004						4345.5				23006	
							4345.1	23008				
4344.5	23011	3d										
4344.3				23012	2d							
							4343.2				23018	1vd
4342.1	23024			23024			4342.6	23021	5d			
							4341.5				23027	
							4341.1	23029				
4340.6	23032	4d		23032	3d		4339.3	23039	6d			
							4338.9				23041	3vd
4309.0	23201											
4307.5	23209	2d					4307.7	23208				
							4304.9	23223	1vd			
4296.0				23271			4296.5	23268				
4295.8	23272											
4294.9				23277	6s	6s 8s						
4294.7	23278	6s										
							4293.6	23284	4d			

Table III. (Continued)

	Liquid N_2 temp.							Room temp.				
	conglomerate			single crystal				conglomerate			crystal	
A	cm.$^{-1}$	I	T	cm.$^{-1}$	I	P	A	cm.$^{-1}$	I	T	cm.$^{-1}$	I
4275.2				23384								
4275.0	23385						4274.9	23386				
4274.5				23388	10s	10d 10s	4274.7				23387	
4274.3	23389	10s										
4273.9				23391								
4273.8	23392											
4273.0				23396	10s	10d 10s						
4272.9	23397	10s										
							4272.3				23400	10s
							4271.9	23402	10s			
4264.3	23444											
4263.9				23446								
							4262.3	23455				
4258.8				23474	1vd		4258.7	23475	1vd			
4258.3	23477	1vd										
							4254.7	23497				
4253.9				23501								
4253.8	23502											
4248.5				23531	1vd							
4248.3	23532	1vd					4248.2	23533	1vd			
4244.7	23552			23552								
4242.6				23564	1vd							
4241.7	23569	1vd										
4239.5	23581											
4236.1	23600	1vd										
4233.6	23614			23614								
4232.2				23622	1d							
4231.6				23625								
4229.8				23635	1d							

Table III. (Continued)

	Liquid N_2 temp.						Room temp.					
	conglomerate			single crystal				conglomerate			crystal	
A	cm.$^{-1}$	I	T	cm.$^{-1}$	I	P	A	cm.$^{-1}$	I	T	cm.$^{-1}$	I
4229.1				23639								
4228.0	23645	1vd										
4227.3				23649	1d							
4223.8	23669			23669								
							4223.0	23673				
4222.3	23677	4d		23677	4d							
4220.9				23685								
4220.7	23686											
4219.6				23692	4d							
4219.3	23694	4d										
4217.9				23702								
4217.7	23703											
4216.4				23710	6d							
4216.3	23711	6d					4216.3	23711	1vd			
							4211.1	23740				
4208.8	23753											
4208.5				23755								
4206.7	23765	4vd										
4206.3				23767	3vd							
							4205.4	23772	1vd			
4201.9	23792			23792			4201.7	23793				
4199.4	23806	5vd										
4199.3				23807	4vd							
4196.1	23825						4196.3	23824	2vd			
4195.6				23828								
4194.3				23835	3vd							
4194.2	23836	4vd										

Table III. (Continued)

	Liquid N_2 temp.							Room temp.				
	conglomerate			single crystal				conglomerate			crystal	
A	cm.$^{-1}$	I	T	cm.$^{-1}$	I	P	A	cm.$^{-1}$	I	T	cm.$^{-1}$	I
4189.8				23861			4190.3	23858				
4189.6	23862											
4187.8	23872	6d		23872	5vd							
							4185.6	23885	1vd			
4180.5				23914								
4180.3	23915						4180.1	23916				
4178.9	23923	10d										
4178.7				23924	10d	10s 10d						
							4177.2	23933	6d			
4175.6	23942			23942			4175.6	23942				
4174.2	23950	9d		23950	9d	8s 10d						
							4172.6	23959	4vd			
4169.5	23977											
4169.1				23979								
4168.3				23984	4d							
4168.1	23985	5d										
4162.5	24017			24017								
4161.0				24026	1vd							
4160.8	24027	1vd										
4157.7	24045			24045								
4155.6				24057	1vd							
4155.1	24060	2vd										
4151.1	24083											
4150.8				24085								
4148.2	24100	2vd										
4147.5				24104	1vd							
4079.3	24507											
4075.7	24529	2vd										

Table III. (Continued)

Liquid N_2 temp.							Room temp.					
	conglomerate			single crystal				conglomerate			crystal	
A	cm.$^{-1}$	I	T	cm.$^{-1}$	I	P	A	cm.$^{-1}$	I	T	cm.$^{-1}$	I
4072.8	24546											
4072.7				24547								
4071.5	24554	3d		24554	3d							
4027.1	24825											
4026.7				24827								
4025.1	24837	3vd		24837	2vd		4025.0	24838				
4023.8	24845											
4023.5				24847								
4022.5	24853	3vd		24853	2vd							
							4021.4	24860	2vd			
4019.8	24870			24870								
							4019.0	24875				
4018.0	24881	7d		24881	6d							
							4016.9	24894	2vd			
4013.2	24911											
4013.0				24912								
4011.4	24922	4vd										
4011.2				24923	4vd							
							4010.7	24926	0vd			
3823.9	26144											
							3823.2	26149				
3822.3	26155	?										
							3820.4	26168	1vd			
3814.1				26211			3814.4	26209				
3813.8	26213											
3812.9				26219	6d	5d 1d						
3812.8	26220	6d										
							3810.3	26237	3vd			

Table III. (Continued)

	Liquid N_2 temp.							Room temp.				
	conglomerate			single crystal				conglomerate			crystal	
A	cm.$^{-1}$	I	T	cm.$^{-1}$	I	P	A	cm.$^{-1}$	I	T	cm.$^{-1}$	I
3804.4	26278			26278			3804.1	26280			26280	
3803.8				26282	10s	7s 10s						
3803.7	26283	10s										
							3802.4	26292	8s			
							3802.1				26294	5s
3796.9	26330			26330			3796.7	26331				
3796.2	26335	8s		26335	8s	0 5s						
							3794.9	26344	2d			
3756.4	26614											
3754.7	26626	1vd										
3752.5	26641											
3751.0	26652	2vd										

Table IV. Absorption lines of Nd_2O_3

Liquid N_2 temp.				Room temp.			
A°	cm.$^{-1}$	I	T	A°	cm.$^{-1}$	I	T
				8503.9	11756		
				8484.8	11783	5vd	H
				8436.8	11850		
				8424.1	11867	5d	H
				8407.1	11891		
				8395.0	11909	4d	H
				8350.7	11972		
				8326.0	12007	5vd	H
8323.2	12011						
8314.0	12025	1vd	L				
				8287.8	12063		
8279.0	12075						
8270.7	12088	9vd	L				
8267.1	12093						
				8260.4	12103	10vd	HL
8259.3	12104	9vd					
8235.8	12139			8236.1	12138		
8228.8	12149	10d					
8225.5	12154						
8216.9	12167	10d					
				8213.0	12172	10vd	HL
8212.1	12174						
8205.6	12183	10d					
8192.5	12203						
8188.5	12209	9s					
				8179.8	12222		
8178.8	12223						
8163.7	12246	10vd	L				
8155.4	12258						
8141.8	12279	10vd					
				8139.2	12283	10vd	
8130.2	12296						
8121.7	12309	6vd					
8112.3	12324						
8107.4	12331	10s	L				
8098.8	12344						
8092.1	12354	10d					
				8090.8	12356		
8085.6	12364						
8074.2	12382	10d					
8065.5	12395						
				8059.7	12404	10vd	
8059.1	12405	9d	L				

Table IV. (Continued)

Liquid N_2 temp.				Room temp.			
A °	cm.$^{-1}$	I	T	A°	cm.$^{-1}$	I	T
8045.0	12427						
8042.0	12431	2d					
8036.2	12440						
8030.7	12449	5s					
8020.1	12465						
8014.4	12474	5s					
8006.9	12486						
8003.3	12491	2d					
				7994.4	12505		
7993.2	12507						
7989.2	12513	10s					
7981.2	12526						
7970.0	12544	9d					
7959.5	12560						
				7950.0	12575	10vd	
7949.0	12578	9d					
7935.7	12598						
7928.2	12610	3vd					
7920.0	12623			7920.3	12622		
7907.7	12642	3vd					
				7905.8	12645	6d	
7864.8	12711						
7861.8	12716	8s					
7836.4	12757						
				7827.5	12772		
7822.7	12780	1vd					
				7812.4	12797	6d	
7786.1	12840						
				7785.1	12842		
7783.2	12845	2s					
				7775.7	12857	8d	H
				7766.2	12873		
				7750.9	12898	8d	H
7741.0	12915						
7731.5	12931	2vd					
				7690.2	13000		
7671.3	13032						
				7661.2	13049	9vd	HL
7660.6	13050	8d					
				7637.7	13089		
7635.1	13094						
7628.0	13106	9d	L				
7622.4	13116						
7608.5	13140	10d	L	7608.9	13139	10vd	

Table IV. (Continued)

Liquid N_2 temp.				Room temp.			
A°	cm.$^{-1}$	I	T	A°	cm.$^{-1}$	I	T
7590.3	13171						
7582.5	13185	8d					
				7563.4	13218		
7560.9	13222						
7547.2	13246	10d					
7541.0	13257						
7530.5	13276	10d	L				
				7529.8	13277	10vd	HL
7519.3	13297						
7511.8	13309	10s					
7507.2	13317						
7504.1	13322	10s					
7501.8	13326						
				7500.0	13330		
7498.8	13332	10s					
7496.1	13337						
7489.6	13348	10d					
7481.4	13363						
7475.7	13373	8d					
7474.1	13376						
				7465.7	13391	10vd	HL
7465.0	13392	8d					
7442.2	13433						
7438.4	13440	9s					
7431.8	13452						
7427.3	13460	2vd					
7413.4	13485						
7406.7	13498	0	L				
7388.5	13531						
7379.8	13547	5vd					
				7358.0	13587		
7352.4	13597						
7350.3	13601	10vs	L	7350.8	13600	2vd	
7348.3	13605						
7346.1	13609	5s	L				
				7342.0	13617		
7339.3	13621						
7333.4	13632	1vd					
				7327.3	13644	1vd	
				7313.4	13670		
7309.0	13678						
7301.4	13692	1vd		7301.0	13693	1vd	
7296.5	13701						
7287.0	13719	1vd					

Table IV. (Continued)

Liquid N_2 temp.				Room temp.			
A°	cm.$^{-1}$	I	T	A°	cm.$^{-1}$	I	T
7264.3	13762						
7261.5	13767	1vd					
				7166.5	13950		
				7153.3	13976	1vd	H
				7085.2	14110		
				7068.1	14144	3vd	H
				7042.7	14195		
7040.4	14200						
7034.2	14212	0	L				
				7026.3	14228	5vd	H
				6997.2	14287		
6995.7	14291						
6989.4	14303	4d					
				6985.0	14312	3vd	
				6969.8	14344		
6964.1	14355						
				6961.4	14361	5d	
6960.3	14363	9s	L				
				6955.4	14373		
6952.5	14379						
6947.5	14390	10d	L				
				6945.6	14394	10d	
6929.4	14427						
6925.7	14435	2d					
				6922.6	14442		
6918.2	14451						
6914.0	14459	10d	L				
6911.0	14466						
6907.0	14474	4d	L	6907.5	14473	9d	
6894.1	14501						
6889.9	14510	2vd					
				6882.3	14526		
6880.7	14529						
6875.7	14540	4vd					
6868.2	14556						
				6867.3	14558	4vd	
6863.2	14566	8s					
6853.1	14588						
				6850.7	14593		
6849.0	14597	3d					
6841.4	14613						
				6839.2	14618	1vd	
6836.7	14623	5d					

Table IV. (Continued)

Liquid N_2 temp.				Room temp.			
A°	cm.$^{-1}$	I	T	A°	cm.$^{-1}$	I	T
6826.8	14644						
				6825.6	14647		
6822.5	14653	1vd					
6818.2	14663						
6812.7	14674	1vd					
6807.9	14685						
				6807.2	14686	1vd	
6804.5	14692	1vd					
				6500.6	15379		
				6489.0	15406	1vd	H
				6483.2	15420		
				6472.9	15445	1vd	H
				6469.7	15452		
				6460.3	15475	1vd	H
				6438.7	15527		
				6428.1	15552	3vd	H
6414.7	15585						
6409.3	15598	1vd					
6403.3	15613			6403.2	15613		
6400.0	15621	3d		6399.8	15621	3d	
				6394.4	15634		
6393.0	15638						
6390.6	15644	9s	L				
				6390.0	15645	9d	L
				6387.1	15652		
6386.4	15654						
6383.5	15661	2d		6383.9	15660	5vd	
				6376.0	15679		
6374.7	15683						
6371.5	15691	9s	L	6371.8	15690	7s	L
				6367.0	15702		
6365.5	15705						
				6364.0	15709	2vd	L
6362.5	15713	4d	L				
				6343.9	15759		
6341.9	15764						
				6340.3	15768	5s	
6339.1	15771	7d					
				6333.3	15785		
6332.7	15787						
6329.6	15794	10s	L				
				6327.8	15799	10d	L

Table IV. (Continued)

Liquid N_2 temp.				Room temp.			
A°	cm.$^{-1}$	I	T	A°	cm.$^{-1}$	I	T
				6324.1	15808		
6323.9	15809						
6319.1	15821	4vd					
				6318.3	15823	10d	
				6305.8	15854		
6303.2	15861						
				6300.5	15867	8d	
6299.5	15870	8d					
6294.4	15883						
				6293.3	15886		
6291.4	15890	1d					
6290.0	15894						
				6287.8	15899	10d	
6286.9	15902	10d					
6276.7	15928	0					
6273.8	15935						
6269.4	15946	1vd					
				5536.7	18056		
				5531.4	18074	5d	H
				5521.7	18105		
				5516.6	18122	5d	H
				5496.0	18190		
				5489.2	18213	5d	H
				5463.8	18297		
5462.2	18303						
5458.0	18317	5d	L	5457.5	18318	8d	L
				5449.2	18346		
5446.0	18357						
5442.5	18369	5d	L	5442.6	18368	8d	L
				5424.4	18430		
5420.7	18443						
5416.2	18458	3d	L	5416.9	18456	8d	L
5414.1	18465						
				5413.4	18468		
5409.6	18481	10d					
				5408.4	18485	8d	
				5401.7	18508		
5400.5	18512						
5396.9	18524	10d					
5394.6	18532						
5391.6	18542	10d		5392.1	18541	10d	
5387.9	18555						
5385.6	18563	10s					

Table IV. (Continued)

Liquid N_2 temp.				Room temp.			
A°	cm.$^{-1}$	I	T	A°	cm.$^{-1}$	I	T
				5383.7	18569		
5381.4	18577						
				5378.6	18587	8d	
5377.0	18593	10d					
				5376.2	18595		
5373.2	18606						
5367.9	18624	10d		5368.1	18623	10d	
				5364.6	18636		
5356.5	18664						
5352.4	18678	10d					
				5354.2	18672	8d	
				5351.3	18682		
				5343.7	18708	10d	
5348.5	18692						
5337.7	18729	10d					
				5331.0	18753		
5325.7	18772						
				5321.6	18786	4vd	
5317.1	18802	3vd					
				5306.9	18838		
5305.2	18844						
5297.2	18873	4vd		5297.1	18873	5vd	
5291.6	18893						
5289.2	18901	1d					
5282.6	18925			5282.9	18924		
5277.8	18942	7d					
5275.6	18950						
5271.4	18965	7d					
				5268.9	18974	6vd	
5268.0	18977						
5264.2	18991	6s					
				5262.7	18996		
5261.7	19000						
5258.3	19013	6s					
				5256.1	19020	6vd	
5249.4	19045						
5245.4	19059	6d					
5241.6	19073			5242.0	19071		
5236.3	19092	10s		5236.5	19091	8d	
5232.6	19106						
5230.0	19115	2d					
5224.0	19137						
5213.1	19177	10vd					

Table IV. (Continued)

Liquid N_2 temp.				Room temp.			
A°	cm.$^{-1}$	I	T	A°	cm.$^{-1}$	I	T
				5219.4	19154		
				5210.4	19187	9d	
5206.2	19203						
5202.6	19216	9vd		5202.7	19215		
5199.5	19227	10vd		5197.8	19234	7d	
5194.8	19245			5191.2	19258		
5190.4	19261						
				5186.2	19277	7d	
5185.3	19280	10d					
5150.4	19411	0					
				5123.4	19513		
5120.3	19525						
5113.8	19550	5vd					
				5113.1	19552	1vd	
5075.4	19697						
5068.5	19724	3vd					
				4985.5	20053		
				4980.0	20075	4d	
4968.4	20122						
				4967.4	20126		
4965.7	20133	4s					
				4963.3	20142	4d	
4938.3	20244						
				4937.7	20247		
4935.9	20254	5s		4930.7	20275	1vd	H
				4927.0	20291		
				4921.5	20313	1vd	
				4910.0	20361		
				4899.0	20407	1vd	H
				4887.2	20456		
4885.7	20462						
4882.3	20476	5d					
				4881.6	20479	7d	
4876.3	20502						
				4874.0	20511		
4873.1	20515	4d	L				
				4867.7	20538	9d	
4870.0	20528						
4867.4	20539	10s					
4864.4	20552						
4862.2	20561	3s					
4860.6	20568						
4858.6	20576	4s					

Table IV. (Continued)

Liquid N_2 temp.				Room temp.			
A°	cm.$^{-1}$	I	T	A°	cm.$^{-1}$	I	T
				4857.7	20580		
4855.4	20590						
				4853.8	20597	10d	
4851.7	20606	10d		4851.3	20607		
4894.0	20617						
				4847.6	20623	3d	
4845.7	20631	8d	L				
				4836.6	20670		
4835.9	20673						
4831.7	20691	6d					
				4830.8	20695	8d	
4820.8	20738						
4818.6	20747	3s		4818.4	20748		
4814.7	20764						
				4813.4	20770	8d	
4812.7	20773	10s					
4809.3	20787			4809.0	20789		
4802.9	20815	5d		4802.7	20816	6d	
4794.2	20853						
				4792.7	20859		
				4784.3	20896	9d	
4782.9	20902	10vd					
4775.3	20935						
				4774.3	20940		
				4768.3	20966	2d	
4766.1	20976	8vd					
4728.4	21143						
4725.2	21157	2d					
				4719.1	21185		
4715.9	21199						
4709.9	21226	8vd		4709.6	21227	6vd	
4705.4	21246						
				4704.4	21251		
4699.3	21274	8vd					
				4692.4	21305	6vd	
4685.9	21335			4686.2	21333		
4682.7	21349	4s					
				4682.1	21352	8s	
4680.0	21362			4680.0	21362		
4677.4	21373	10s					
				4676.6	21377	8s	
4673.8	21390						
4671.1	21402	3s					

Table IV. (Continued)

Liquid N_2 temp.				Room temp.			
A°	cm.$^{-1}$	I	T	A°	cm.$^{-1}$	I	T
				4668.9	21412		
4668.1	21416						
4665.9	21426	4s					
				4662.9	21440	2vd	
4660.7	21450	0					
4521.6	22110						
4501.4	22209	1vd					
4477.0	22330						
				4472.1	22355		
				4468.8	22371	8s	N
4464.3	22394	1vd					
				4424.7	22594		
4422.4	22606						
4419.1	22623	5d	L	4419.6	22620	10d	L
4390.9	22768			4390.7	22769		
4388.0	22783	7s					
				4387.4	22786	7s	
				4381.1	22819		
4379.5	22827						
				4378.2	22834	10s	
4376.3	22844	10s					
				4375.1	22850		
4374.1	22855						
				4371.8	22867	10s	
4370.7	22873	10s					
4366.7	22894						
4364.6	22905	3s					
4362.1	22918						
				4361.5	22921		
4359.5	22932	3s					
4357.0	22945						
4354.2	22960	3s		4354.9	22956	2vd	
4334.8	23063			4335.2	23061		
				4328.0	23099	0	
4326.1	23109	1vd					
4311.9	23185						
				4310.3	23194		
4308.7	23202	3s					
4306.0	23217						
4303.1	23233	3s		4303.6	23230	1vd	
4300.3	23248						
4298.1	23260	5s					
				4246.8	23541		
4244.7	23552						
4238.8	23585	2d		4238.3	23588	1vd	

The thicker the sample used, whether conglomerate or single crystal, the greater the number of lines observed due to the increased length of path which the light must travel. Also, at the temperature of liquid nitrogen the lines were much sharper and better resolved. At this temperature the lines of both salts underwent a slight shift, which in the case of the bromate was on the order of 10 cm.$^{-1}$ to the red, while in the oxide a slight shift to the violet was noted.

Making use of the chart described on page 35 above, it was found that certain wave number intervals, showing the temperature dependence as described in section IIA above, occurred a number of times indicating the existence of energy levels at these intervals above the basic state.

In certain cases the long wave length lines banded together and were not resolved at room temperatures. Where these lines were used in selecting intervals the high frequency line is primed indicating that it falls inside a band envelope. Owing to thermal broadening and variation in selection rules, some of the lines may be "washed out" at high temperatures. Several of the reasons for thermal broadening are: (a) as the temperature increases the atoms begin to oscillate, causing the atoms to be subjected to various fields and therefore shifting the positions of the lines, and since on a photographic plate an integrated effect of a large number of transitions is observed the result is a broadened line; (b) the effective width of the basic state increases due to the vibrational and oscillational levels of the basic state coming into importance as the temperature is increased; (c) the upper states of many absorption lines may lie above broad "metallic" type states. At low temperatures there will be very little resonance between these states so that the upper states will have a long life-time and have a very sharp energy breadth. As oscillation of the atoms takes place with increasing temperature the wave functions of these states will scramble due to the perturbations. The life-time of the states will accordingly become much shorter and their energy less well defined. Transitions terminating in these levels will accordingly appear broad. In some cases it was necessary to measure from the high temperature position of the line to the low temperature position of the other line. These cases are marked with an asterisk (*). Several of the 380 cm.$^{-1}$ levels had to be measured from low temperature position to low temperature because of the above effect and in these instances the lines are marked with a double asterisk (**).

A cross check on the value of an interval may be found by observing the temperature at which a line appears and then calculating the interval by means of the Boltzmann relation.

All intervals chosen were well within the estimated experimental error for the region in which they were located.

The estimated accuracy for the various lines are as follows: "s" lines 1 cm.$^{-1}$; "d" lines 2 cm.$^{-1}$; "vd" lines 5 to 10 cm.$^{-1}$; lines of intensity 7 to 10,1 cm.$^{-1}$; intensities of 3 to 6, 3 to 5 cm.$^{-1}$; intensities of 0 to 2, 5 to 10 cm.$^{-1}$.

Table V. Evidence for 116 cm.$^{-1}$ interval of neodymium bromate

12388 - 12274 = 114
12502 - 12388 = 114
12573 - 12457 = 116
12971 - 12856 = 115
12996 - 12883 = 113
13086 - 12971 = 115
13109 - 12996 = 113
13428 - 13312 = 116
13547 - 13428 = 119
13606 - 13488 = 118
13871 - 13753 = 118
13894 - 13773 = 121
13960 - 13841 = 119
14778 - 14658 = 120
14824 - 14709 = 115
14837 - 14722' = 115
14845 - 14730' = 115
14855 - 14741 = 114
14893 - 14778 = 115
15921 - 15800 = 121
15985 - 15870' = 115
15989 - 15874' = 115
16037 - 15921 = 116
16045 - 15930 = 115

16073 - 15956 = 117
18898 - 18780 = 118
18948 - 18829 = 119
19017 - 18998 = 119
19097 - 18979 = 116
19132 - 19017 = 115
19163 - 19047 = 116
19564 - 19449 = 115
19587 - 19468 = 119
19605 - 19491 = 114
19654 - 19540 = 114
19718 - 19605 = 113
20705 - 20588 = 117
21152 - 21038 = 114
21170 - 21055 = 115
21190 - 21075 = 115
21576 - 21460 = 116
23673 - 23559 = 114
23707 - 23590 = 117
23760 - 23644 = 116
23919 - 23799 = 120
23946 - 23831 = 115
23981 - 23867 = 114
26332 - 26216 = 116

Mean Interval : 116

Table VI. Evidence for a 380 cm.$^{-1}$ interval in neodymium bromate

14851 - 14473 = 378
14895 - 14515 = 380
15989 - 15614 = 375
16037 - 15657' = 380*
16045 - 15665' = 380*
16056 - 15676' = 380*
16074 - 15694' = 380*
19134 - 18753 = 381**
19163 - 18780 = 383**
21170 - 20790' = 380*
21189 - 20809' = 380*

Mean Interval: 380

Table VII. Evidence for a 245 cm.$^{-1}$ level in neodymium oxide

12018 - 11770 = 248*
12099 - 11858 = 241*
12144 - 11900 = 244*
12234 - 11989 = 245*
12327 - 12083 = 244*
12400 - 12155 = 245*
13100 - 12850 = 250
13128 - 12885 = 243
13267 - 13024 = 243
13492 - 13248 = 244
13599 - 13354' = 245*
13607 - 13362' = 245*
14206 - 13963 = 243
14359 - 14114 = 245
14384 - 14139 = 245
14455 - 14211 = 244
15639 - 15393 = 246
15684 - 15433 = 251
15709 - 15464 = 245
15790 - 15540 = 250
15898 - 15656 = 242
18308 - 18065 = 243
18357 - 18113 = 244
18443 - 18201 = 242*
20508 - 20261 = 247
20624 - 20384 = 240*

Mean Interval : 245

The praseodymium present in the sample of neodymium used had its advantages and disadvantages. This sample of salt was used rather than obtaining a pure sample of neodymium because it allowed us to study the effect on the praseodymium ion of the neodymium bromate and oxide fields and also rendered a check as to whether a level was electronic or vibrational in character, since a vibrational level should occur for both ions.

In the following paragraphs a description of the spectra is given by multiplets.

Near infra-red multiplets

The spectra of both salts seems to be superimposed on a continuous background of absorption. The lines in nearly all cases are extremely fuzzy along the edges. Only in the case of the polarized spectra of the bromate were any real sharp lines observed, and even there many of the lines were broad and diffuse. For these reasons few constant intervals can be definitely assigned in these ranges.

Quantum theory predicts that if the electronic states have certain properties they should strongly couple with the vibrational and oscillational energies of the neighboring atoms and lattice frequencies. This will give rise to an overlapping of the electronic multiplets with a weak molecular type spectra which at higher temperatures and under low resolving power will tend to give an envelope of absorption underlying the electronic multiplet. The relative intensity of these "associated" lines or continuum appears to be at a maximum in these multiplets and at a minimum in the 6800A and 6400A multiplets.

6800 A. and 6400 A. multiplets

These multiplets are the cleanest cut of the entire spectra, the lines for the most part are well defined. Constant intervals are easily obtained from these regions. Also the polarization spectra in these regions are very clear cut. These two multiplets were the most fruitful of the entire spectra. (See Figs. 6 and 7).

5300 A. multiplets

Due to the intense absorption of the salts in this region it was necessary to use very thin samples in order to obtain the structure of the multiplets. The polarization spectra were of great help in establishing the structure of the bands in this region in the case of the bromate.

4900 A. and 4300 A. multiplets

As a result of the presence of praseodymium in the sample the lines in these regions can not be too definitely assigned to neodymium. All lines found in these regions are reported unless they have been definitely assigned to praseodymium. These were not necessary for the thesis but might be useful sometime and are therefore given.

It was noted that the intensities of the bands varied greatly from multiplet to multiplet. This was to be expected. All the sharp lines are forbidden in the gas spectra unless extremely thick layers are used. It must be borne in mind that there are as many absorbers of light in a millimeter of a solid as there are in several meters of a gas. Therefore these so called forbidden lines, having low probability of transition, show up in the solids. Some of these multiplets are much more "highly" forbidden than others and as a result much thicker layers are required to bring them out.

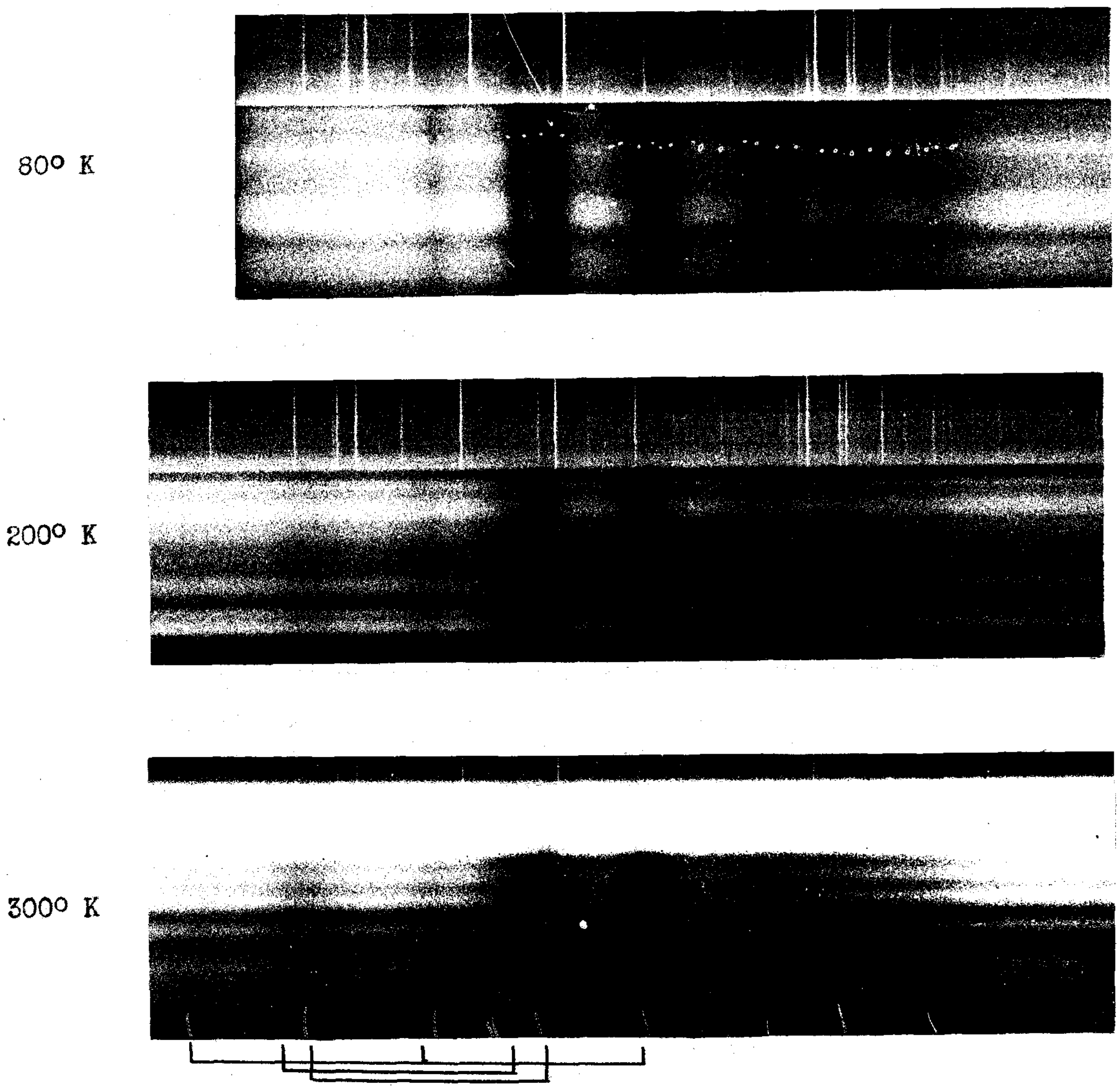

Fig. 6. Temperature effect in the 6800 A multiplet of neodymium oxide. Enlargements from three meter grating plates. Lines fade out as the population of upper states decreases with lowered temperatures.

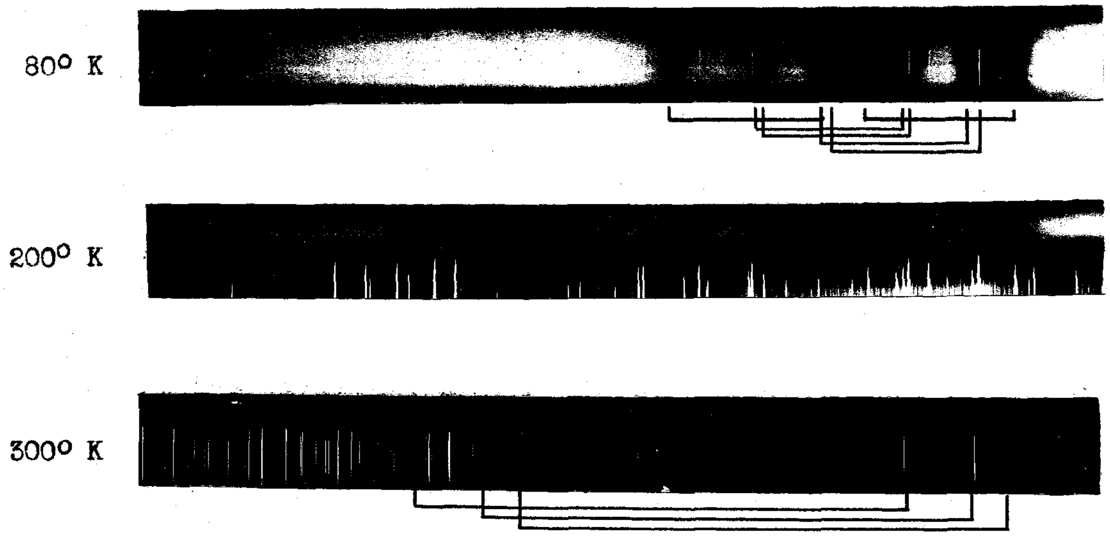

Fig. 7. Temperature effect in the 6300 A multiplet of neodymium bromate. Contact prints from twenty-one foot grating plates. Lines fade out as the population of upper states decreases with lowered temperatures.

V. DISCUSSION

The recurring frequency intervals recorded in Tables V to VII were obtained by use of the two methods outlined in Section IIA. Therefore, only such intervals were considered valid as showed marked intensification of the low frequency line at the higher temperature. In the case of the 245 cm.$^{-1}$ and 380 cm.$^{-1}$ levels (see Figs. 6 and 7) the Boltzmann distribution nearly precludes the occurrence of the low frequency line at the temperature of liquid nitrogen. All intervals chosen as evidence for these levels either showed no low temperature line at the low frequency end or showed a very weak line. Lines chosen as evidence for the 115 cm.$^{-1}$ level showed the temperature dependence.

In addition to these fairly large and clearly defined intervals, some evidence was found for smaller intervals of about 20 cm.$^{-1}$, 30 cm.$^{-1}$, 40 cm.$^{-1}$ and other such values recurring frequently throughout the spectra. It seems highly probable that these small constant frequency differences arise from vibrational frequencies superimposed on the electronic states. Vibrational frequencies should be a function of the mass of the atoms (a constant) and the force constants between them. Due to the fact that the 4f electrons are somewhat shielded from the influence of neighboring groups by the completed 5s and 5p shells, the force constants should not be affected much by the electronic states and therefore should not differ much from state to state, so that to a first approximation the superimposed vibrational frequencies would be the same for each electronic level.

However, these frequencies should suffer slight modification in so far as the various energy states influence the force constants. Therefore these intervals should not be exactly constant but should fluctuate around certain values.

The number of lines in a multiplet, in general, seems to depend on the thickness of the absorbing layer; the thicker the sample the more lines are observed. This agrees with the conception that many of the lines are due to vibrational and crystal frequencies and not to crystal splitting alone.

In Figure 8, a tentative energy diagram is drawn up for the 16,000 cm.$^{-1}$ multiplet of the bromate incorporating the results obtained. From the temperature dependence of the lines concerned throughout the various spectra, the levels at 0, 116 and 380 cm.$^{-1}$ are attributed to electronic transitions.

In general, lines which are attributed to transitions between electronic states are much more intense than vibrational lines. Vibrational levels show some correlation from salt to salt if the anions in the salts are the same. Electronic transitions in their fine structure differ markedly from salt to salt since these levels depend to a great extent on the fields present in the crystal. In spite of these general rules great care must be exercised in attributing a line to a pure electronic transition. Occasionally a vibrational line will appear as strong as an electronic line but this may be ascribed to some peculiar circumstance or resonance. From theory the symmetry of the neighboring ions about a given ion can be determined from the number of lines and their relative

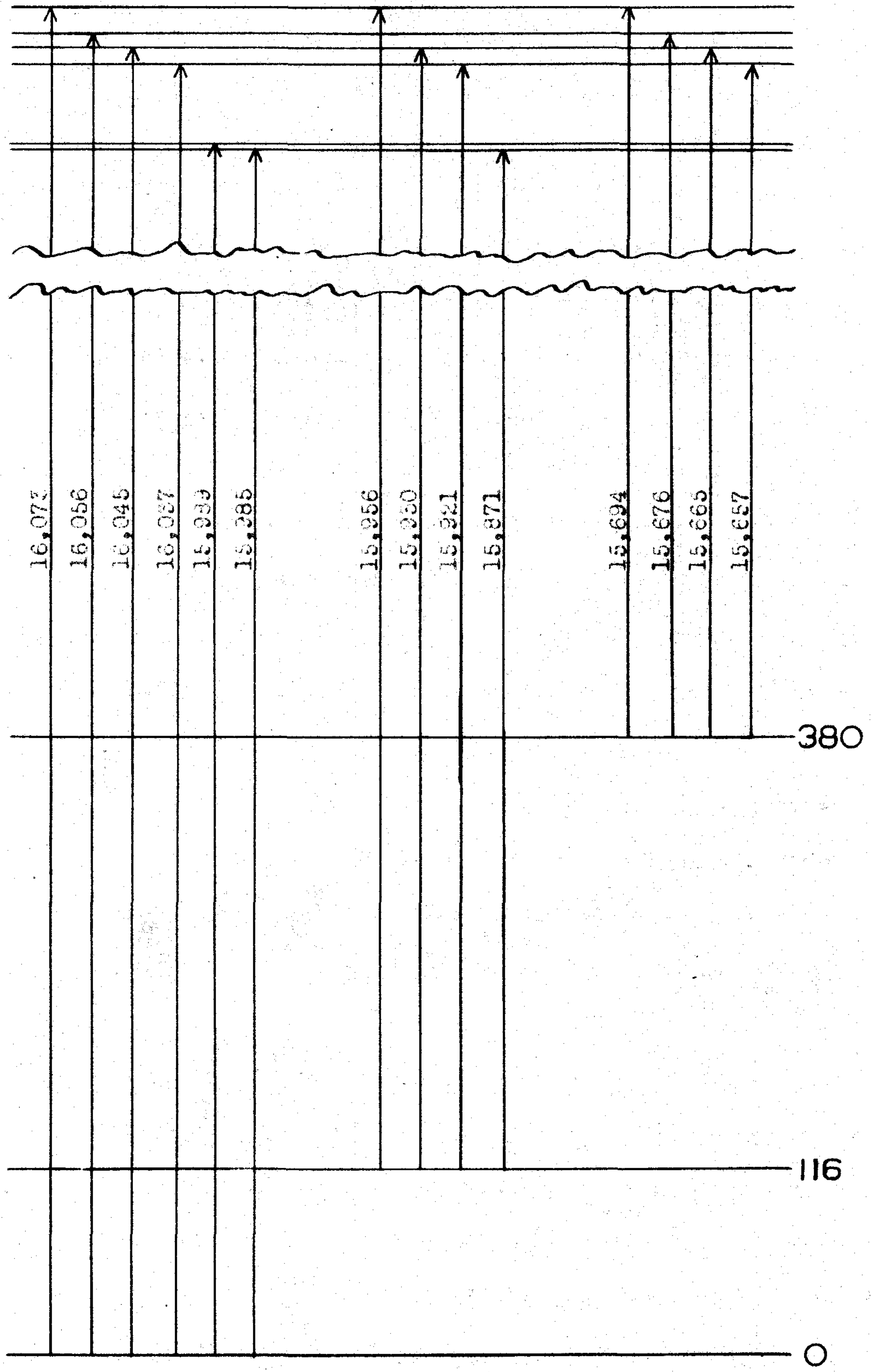

Fig. 8. Partial energy level diagram for the trivalent Nd ion in neodymium bromate nonahydrate.

spacings into which a given term is split. It is dangerous to draw any conclusions about the fields surrounding an ion from the number of lines without making a thorough investigation of the spectra, since the extra lines from intensified vibration may give erroneous ideas.

Following the method of Penney and Schlapp, as outlined in Section IIB above, the theoretical curve for the variation of magnetic susceptibility of neodymium oxide with temperature was calculated. Figure 9 shows this curve as compared with the experimental points of other workers (49,50,51,52,53). Theagreement between the experimental points and the calculated curve is very satisfactory up to fairly high temperatures where the higher levels start to come into the calculations. Also Miss Frank (31) has shown that at room temperatures it is necessary to add about three percent to the susceptibility to correct for the $J = 11/2$ multiplet.

The specific heats due to electronic vibration were calculated using the equation as developed by Giaque (42) and described in Section IIC. Since only the lower electronic level for neodymium oxide was found experimentally from the spectra it was necessary to calculate the higher level by means of the energy level equations of Penney and Schlapp (12). This level was calculated to occur at 839 $cm.^{-1}$. The calculated curves for the electronic specific heats versus temperature are given in Figures 10 and 11. These curves agree well in shape and height of maximum with those calculated by Miss Frank for samarium (43). It would be nice to compare these values with experimental results but as yet these salts have not been reported.

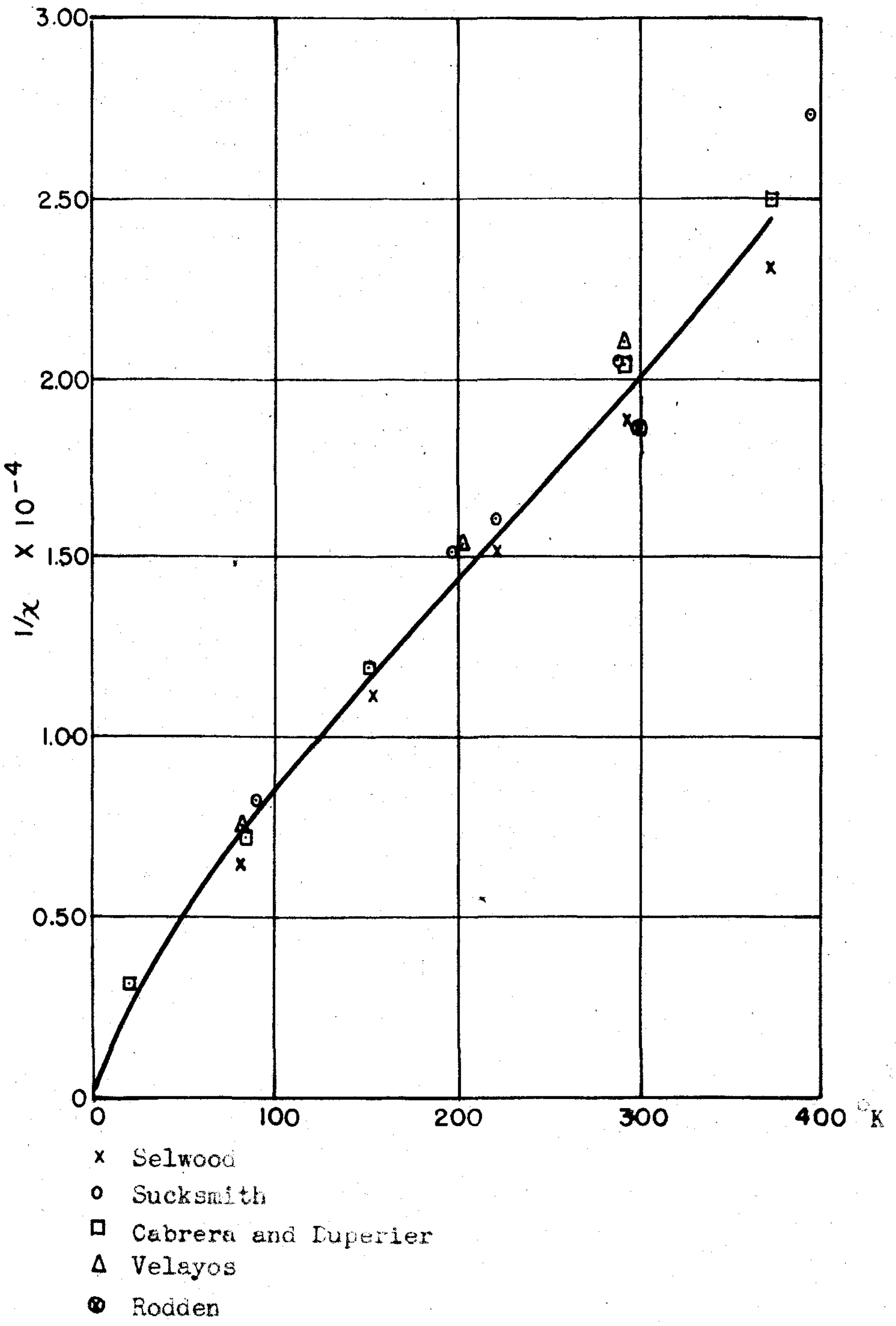

Fig. 9. Calculated magnetic susceptibility of neodymium oxide compared with experimental values.

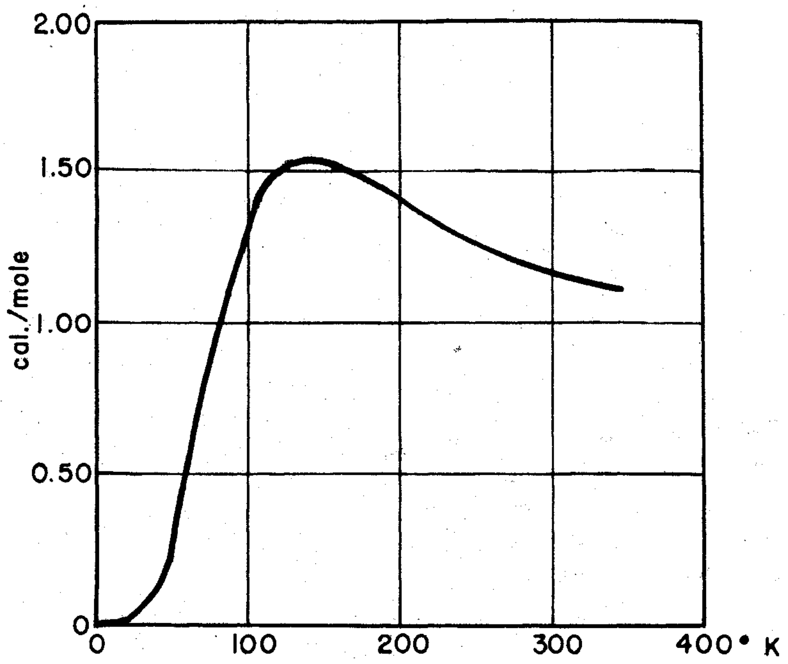

Fig. 10. Electronic specific heat of neodymium oxide.

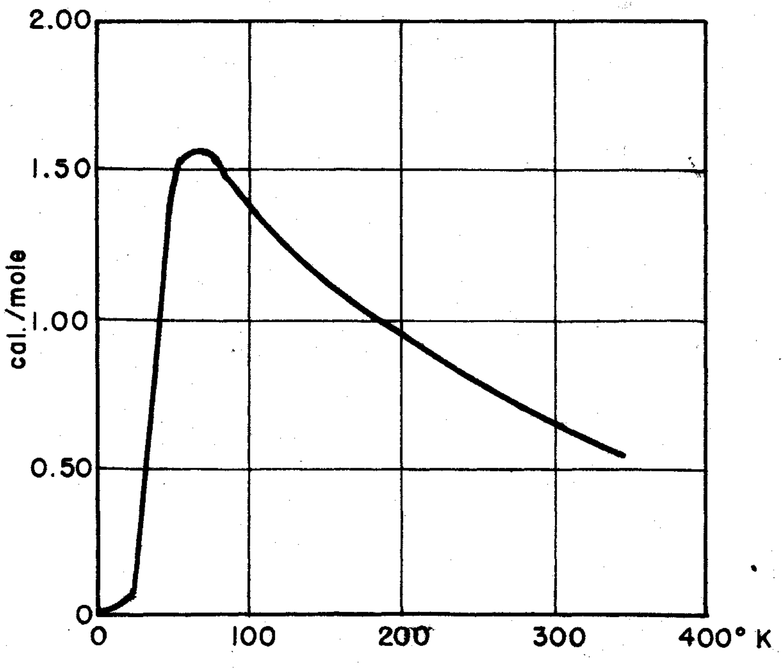

Fig. 11. Electronic specific heat of neodymium bromate.

VI. SUMMARY AND CONCLUSIONS

Pure samples of $Nd(BrO_3)_3.9H_2O$ and Nd_2O_3 were prepared and their absorption spectra examined at various temperatures.

It was found that the absorption lines became sharper and more finely resolved as the temperature was lowered. The bromate suffered a shift of the order of 10 cm.$^{-1}$ to the red at nitrogen temperatures.

Electronic levels were found at 0, 116 and 380 cm.$^{-1}$ for the bromate and 0 and 245 cm.$^{-1}$ for the oxide. Evidence for vibrational levels located at about 20, 30 and 40 cm.$^{-1}$ intervals was noticed.

Calculation of the magnetic susceptibility from the levels obtained yielded good agreement with experimental data.

Theoretical predictions on electronic specific heat have been made and can be checked when experimental results are available.

VII. LITERATURE CITED

(1) Bunsen, Pogg. Ann. 128, 100 (1866).

(2) Becquerel, Compt. rend. 144, 1032 (1907). 145, 795, 1412 (1907).

Becquerel and Onnes, ibid. 146, 625 (1908).

Becquerel, Onnes and de Haas, ibid. 181, 758 (1925).

(3) Freed and Spedding, Nature 123, 525 (1929).

(4) Freed and Spedding, (a) Phys. Rev. 34, 945 (1929), (b) J. Am. Chem. Soc. 52, 3747 (1930).

(5) Bethe, Ann. Physik 3, 133 (1929). Z. Physik 60, 218 (1930).

(6) Becquerel, (a) J. Phys. Radium 10, 313 (1929), (b) Z. Physik 58, 205 (1929).

(7) Spedding and Bear, Phys. Rev. 39, 948 (1932).

(8) Spedding and Bear, ibid. 42, 58, 76 (1932). 44, 287 (1933). 46, 308, 975 (1934).

(9) Spedding and Nutting, J. Am. Chem. Soc. 55, 496 (1933).

(10) Ephraim and Ray, Ber. 62B, 1520 (1929).

(11) (a) Spedding, Hamilin and Nutting, J. Chem. Phys. 5, 191 (1937).

(b) Spedding and Hamlin, ibid. 5, 429 (1937).

(12) Penney and Schlapp, Phys. Rev. 41, 194 (1932).

(13) Gorter, "Paramagnetische Eigenschaften von Salzen," Doctoral Dissertation, Leiden, 1932.

(14) Van Vleck, Phys. Rev. 31, 587 (1928).

(15) Meyer, Phys. Z. 26, 51 (1925).

(16) Zernicke and James, J. Am. Chem. Soc. 48, 2827 (1926).

(17) Ewald, Ann. Physik 34, 207 (1939).

(18) Spedding, J. Chem. Phys. 5, 316 (1937).

(19) Meehan and Nutting, J. Chem. Phys. 7, 1002 (1939).

(20) Spedding, Howe and Keller, J. Chem. Phys. 5, 416 (1937).

(21) Gobrecht, Ann. Physik 28, 673 (1937).

(22) Hund, Z. Physik 33, 855 (1925).

(23) Lange, Ann. Physik 32, 361 (1938).

(24) Spedding, Moss and Waller, J. Chem. Phys. 8, 908 (1940).

(25) Foster, "Introduction to General Chemistry", p. 424, 1934.

(26) Cabrera, Compt. rend. 180, 668 (1925).

(27) Laporte, Z. Physik 47, 761 (1928).

(28) Van Vleck and Frank, Phys. Rev. 34, 1494, 1525 (1929).

(29) Freed, J. Am. Chem. Soc. 52, 2702 (1930).

(30) Freed and Spedding, Nature 123, 525 (1929).

(31) Frank, Phys. Rev. 39, 119 (1932).

(32) Cabrera, (a) Compt. rend. 207, 1077 (1938), (b) J. Chim. phys. 36, 117 (1939).

(33) Ahlberg and Freed, Phys. Rev. 39, 540 (1932).

(34) Freed, J. Am. Chem. Soc. 52, 2702 (1930).

(35) Freed and Spedding, Nature 123, 525 (1929).

(36) Schottky, Phys. Z. 23, 448 (1922).

(37) Freed and Spedding, Phys. Rev. 34, 945 (1929).

(38) Giauque and Clark, J. Am. Chem. Soc. 54, 3135 (1932).

(39) (a) Woltjer and Onnes, Leiden Rijksuniversiteit. Kammerlingh Onnes laboratorium. Communications 167C, 31 (1923).

(b) Giauque, J. Am. Chem. Soc. 49, 1870 (1927).

(40) (a) Ahlberg and Freed, ibid. 57, 431 (1935).

(b) Ahlberg and Clark, ibid. 57, 437 (1935).

(41) Spedding and Bear, Phys. Rev. 46, 975 (1934).

(42) Giaque, J. Am. Chem. Soc. 52, 4808 (1930).

(43) Frank, Phys. Rev. 48, 765 (1935).

(44) Ahlberg and Freed, J. Am. Chem. Soc. 57, 431 (1935).

(45) Ahlberg, Blanchard and Lundberg, J. Chem. Phys. 5, 552 (1937).

(46) Spedding, Hamlin and Nutting, J. Chem. Phys. 5, 191 (1937).

(47) Spedding, Phys. Rev. 50, 574 (1936).

(48) Spedding and Bear, Phys. Rev. 42, 58 (1932).

(49) Selwood, J. Am. Chem. Soc. 55, 3161 (1933).

(50) Rodden, ibid. 56, 648 (1934).

(51) Velayos, Soc. espan. fis. quim. 33, 5 (1935).

(52) Cabrera and Duperier, Compt. rend. 188, 1640 (1929).

(53) Sucksmith, Phil. Mag. (vii) 14, 1115 (1932).

VIII. BIBLIOGRAPHY

The literature listed below was also referred to during the course of investigation. It is classified under the titles of the sections to which it is relevant.

Spectroscopic

Selwood, J. Am. Chem. Soc. 52, 3112, 4308 (1930). ibid. 53, 1799 (1931).

Freed and Spedding, Phys. Rev. 35, 212 (1930). ibid. 38, 670 (1931).

Spedding, ibid. 50, 574 (1936).

Spedding, J. Chem. Phys. 5, 160, 316 (1937).

Bethe and Spedding, Phys. Rev. 52, 454 (1937).

Gobrecht, Ann. Physik 31, 600 (1938).

Brode, "Chemical Spectroscopy", 1939.

Harrison, Conference on Spectroscopy and its Applications, Massachusetts Institute of Technology, 7th, 1939 (1940).

Magnetic

Van Vleck, "Theory of Electric and Magnetic Susceptibilities", 1932.

Giaque, J. Am. Chem. Soc. 49, 1870 (1927).

Freed and Spedding, Phys. Rev. 38, 670 (1931).

Spedding, Phys. Rev. 38, 2080 (1931). J. Am. Chem. Soc. 54, 2593 (1932).

Spedding, J. Chem. Phys. 1, 144 (1933).

Spedding and Nutting, J. Chem. Phys. 3, 369 (1935).

Foex and Fehrenbach, Compt. rend. 203, 857 (1936).

Materials

Spedding and Bear, Phys. Rev. 44, 287 (1933).

Ephraim and Ray, Ber. 62B, 1520 (1938).

Bommer, Z. anorg. allgem. Chem. 241, 273 (1939).

Pauling, Z. Krist, 69, 415 (1929). ibid. 75, 128 (1930).

Helmholtz, J. Am. Chem. Soc. 61, 1544 (1939).

IX. ACKNOWLEDGMENTS

The author takes pleasure in acknowledging his indebtedness to Dr. F. H. Spedding, whose direction of this work was a constant source of inspiration. He would also take this opportunity to thank his fellow research workers in the Division of Physical Chemistry, who were always glad to lend assistance and offer helpful criticism, and Dr. I. B. Johns, who so kindly gave permission for the use of his micro-analytical equipment.

Thanks are also due to H. N. McCoy whose gift of the neodymium to Dr. F. H. Spedding made possible this work.