

of dilution, entropy, activity and activity coefficients of these solutions at the temperatures of 550 and 600°.

3. Density determinations of 0.5 mole fraction sodium bromide in silver bromide were made between 600 and 620° and may be expressed by the equation, $d^t = 4.311 - 0.0009 t$.

4. It is pointed out that the positive deviation of the results from Raoult's law seem to indicate that changes in interionic forces upon dilution should be considered.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]
**DEFORMATION OF ELECTRON SHELLS. III. THE MAGNETIC
SUSCEPTIBILITY OF NEODYMIUM NITRATE**

BY P. W. SELWOOD¹

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The object of this work, as pointed out in previous papers,² was to investigate the relations existing between the absorption spectra and other properties of certain rare earth salts. It has already been shown that in the case of aqueous solutions of neodymium salts a shift toward the red of the absorption bands with increasing concentration is attended with an increase in the ionic refraction of the neodymium. The purpose of the work here reported was to see whether the magnetic susceptibility of neodymium nitrate suffered a perceptible change as the changes in absorption and refraction were taking place.

Experimental

The magnetic apparatus used resembled the Bauer and Piccard³ modification of Quinckes' capillary rise method. As shown in Fig. 1 the capillary tube C, which was 1 mm. in internal diameter, was placed between the truncated poles of a Weiss electromagnet. The interspace between the poles was 3 mm. During the course of readings the meniscus was always returned to the same position both while the field was applied and while it was off. It was, therefore, not necessary that the field should be uniform, although an investigation showed that it was uniform over a considerable region. The meniscus was observed by means of the telescope A. The magnet was operated with a current of 5.2 amperes, which was sufficient nearly to saturate the iron pole-pieces as is shown in Fig. 2. This procedure is essential if error is not to be introduced from the hysteresis characteristics of the iron.⁴ It also reduces the proportionate error from slight deviations in the current through the magnet.

¹ National Research Fellow.

² Selwood, *THIS JOURNAL*, **52**, 3112, 4308 (1930).

³ Bauer and Piccard, *J. Phys.*, **1**, 97 (1920).

⁴ Sève, *Ann. chim. phys.*, **27**, 425 (1912).

As the susceptibility of most paramagnetic substances is inversely proportional to the absolute temperature, it was necessary to control the temperature of the solution contained in the magnetic field. This was

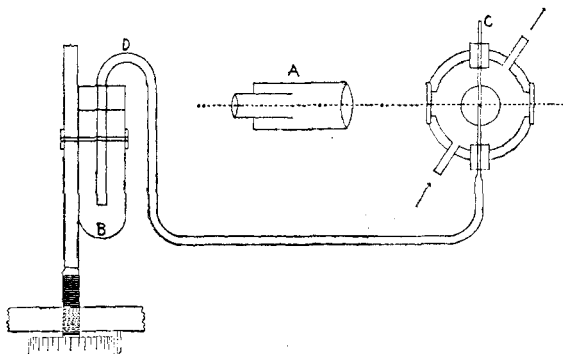


Fig. 1.—Apparatus for measuring magnetic susceptibilities.

done by circulating water from a thermostat constant to 0.1° through a brass collar made to fit snugly between the pole-pieces. Windows were provided for illumination and observation of the meniscus.

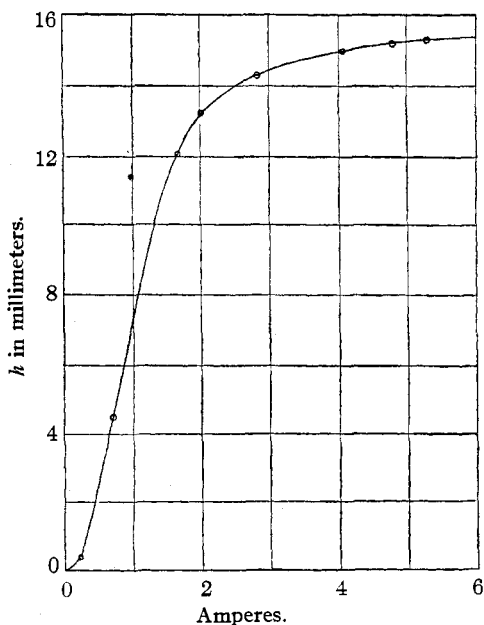


Fig. 2.—Variation of rise of liquid in magnetic field with current through magnet.

The height of the meniscus was controlled by the reservoir B which was mounted on the moving frame of a cathetometer. It was possible by this means to duplicate the setting of the meniscus in the absence of the field to 0.01 mm. As the amount of each solution available was not large, it was necessary to reduce the size of the reservoir until the cross section of the tube D was an appreciable fraction of that of the reservoir. This introduced a slight correction to the change in height of the reservoir, owing to immersion of the tube D. The latter had an internal diameter of 2 mm. In the case of the most concentrated solutions h was about 30 mm.

As great absolute accuracy for the measurements was not essential, the apparatus was calibrated with redistilled water whose mass susceptibility

at 20° was taken as -0.720×10^{-6} .⁵ This indicated a field strength of 26,600 gauss with a current of 5.2 amperes. The mass susceptibility of the solutions was then calculated from the relation

$$X_s = \frac{\frac{2hdg}{H^2} + K_0}{d}$$

where h is the true rise of the solution in the reservoir, d is the density of the solution at 20°, g is the gravitational constant, H is the field strength, and K_0 is the volume susceptibility of air, which is given by Brant as 0.0288×10^{-6} at 20°. For diamagnetic substances the above equation is modified to

$$X_s = \frac{\frac{2hd_1g}{H^2} + K_0}{d}$$

where d_1 is the density of the liquid in the reservoir B, which, however, did not differ from d by more than a fraction of 1%.

The apparent susceptibility of the solute was then calculated from the relation

$$X = \frac{X_s + 0.72(1 - p)10^{-6}}{p}$$

where p is the weight fraction of solute present.

The densities and compositions of the solutions were determined as described in previous communications.

The preparation of pure, neutral solutions of rare earth nitrates is a problem which has heretofore given some difficulty. One of the methods used by the author, which consisted of treating the pure oxide with insufficient acid to effect complete solution, has the disadvantage that the resulting excess hydrated oxide is difficult to remove. The other method, which is the prolonged fractional crystallization of the slightly acid salt from distilled water has the disadvantage that it is difficult to remove the last trace of the acid. This is no doubt due to the high solubility of the rare earth nitrates in water.

The method devised for the present work apparently overcomes both these disadvantages. The neodymium oxide, the preparation of which was described elsewhere, was again treated with hydrogen sulfide, and was precipitated repeatedly as oxalate in order to remove all common elements. The oxide was dissolved in a slight excess of redistilled nitric acid and was then heated for half an hour at 250° under reduced pressure (a few mm. of mercury). This resulted not only in the elimination of all excess nitric acid, but in the complete dehydration of the salt, as determined by analysis. The anhydrous salt was very hygroscopic and gave a clear solution in both water and ethyl alcohol, which is not the case with neodymium nitrate which has been heated until decomposition commences at 280–290°. It

⁵ Brant, *Phys. Rev.*, **17**, 678 (1921).

was found that in the presence of a reducing agent such as alcohol, decomposition of the nitrate took place below 100°. It is believed that this is the first time that anhydrous neodymium nitrate has been prepared. In view of the good solubility of the nitrate in ethyl alcohol, opportunity was taken to measure its magnetic susceptibility in that solvent. The aqueous solutions prepared from the anhydrous salt may be concentrated by slow evaporation without hydrolysis taking place, but if the solution is boiled, a white basic nitrate appears. The solutions so prepared appear to be identical in physical properties with the solutions most carefully prepared by other methods.

Results

The magnetic susceptibilities of the solutions investigated, together with the apparent susceptibility of the anhydrous salt and of the neodymium ion, are given in Table I. The apparent susceptibility of the neodymium suffers a decrease of over 2% in the concentration range 0.3 to 3 molar.

TABLE I

THE MAGNETIC SUSCEPTIBILITY OF NEODYMIUM NITRATE AT 20°				
% Nd(NO ₃) ₃ by weight	Moles per liter	$X_m \times 10^6$	$X_{Nd(NO_3)_3} \times 10^6$	$X_{Nd^{+++}} \times 10^6$ per g. ion
9.33	0.304	0.764	15.2	4980
18.56	.6574	2.223	15.13	4960
26.63	1.016	3.518	15.19	4980
33.57	1.367	4.587	15.09	4950
39.51	1.709	5.499	15.02	4930
45.05	2.068	6.395	15.08	4940
50.36	2.458	7.163	14.93	4900
51.30	2.524	7.303	14.90	4890
53.99	2.738	7.725	14.92	4890
58.04	3.089	8.267	14.76	4880

The susceptibility of the neodymium ion calculated from the molecular susceptibility in the more dilute solutions agrees with the value 4970×10^{-6} found by Decker,⁶ who worked with dilute solutions of the nitrate. Zernike and James,⁷ who worked with the crystalline sulfate octahydrate, obtained a value of 5109×10^{-6} .

In order to find the susceptibility of neodymium nitrate in alcohol solution, it was necessary to measure the susceptibility of ethyl alcohol. The mass susceptibility at 20° was found to be -0.76×10^{-6} . Landolt-Börnstein gives -0.73 for 99% C₂H₅OH to -0.81 for absolute C₂H₅OH.

The susceptibility of a nearly saturated solution of neodymium nitrate in ethyl alcohol, containing 22.57% by weight or 0.6732 mole of Nd(NO₃)₃ per liter, was found to be 2.748×10^{-6} . This gave an apparent value for the neodymium nitrate of 14.9×10^{-6} . In view of the fairly large maxi-

⁶ Decker, *Ann. Physik*, **79**, 324 (1926).

⁷ Zernike and James, *THIS JOURNAL*, **48**, 2827 (1926).

imum probable error in determining the susceptibility of the alcohol, this value for the nitrate cannot be said to differ from the value obtained in aqueous solution.

Discussion of Results

The various measurements made by the author have shown that a relation, as predicted by Foex,⁸ exists between the absorption spectrum, the refraction and the magnetic susceptibility of the neodymium ion. A concentration shift of the absorption bands toward the red is attended with an increase in refraction and a decrease in magnetic susceptibility. In view of the poor development of magnetochemical theory, and the fact that practically no work has been done on the theoretical investigation of rare earth absorption spectra, it scarcely seems possible to present an interpretation of the author's results in terms of atomic structure. It may not, however, be out of place to offer a few general remarks on the subject.

In general, the effective part of a magnetic ion is capable of independent change of orientation so far as its neighbors can influence it. That is, the magnetic susceptibility is not related to the closeness of association of the positive and negative ions as is, for instance, the dielectric constant. It is reasonable to suppose, however, that the combined influence of neighboring ions in concentrated solutions and especially in crystals would produce a field which would in some way affect the mean susceptibility of the active ion.

Owing to the difficulty of preparing the pure rare earths, it is important that comparisons of the susceptibility of different compounds of the same element should be made by the same investigator using the same materials. Unfortunately, few such measurements are available. St. Meyer,⁹ who examined several salts of neodymium, does not give the individual results; but in the table given by Zernike and James⁷ it is evident that the susceptibility of neodymium in the oxide has consistently been found to be lower than in the sulfate. That is a result which might be expected if the closeness of atomic binding has anything to do with the magnetic susceptibility.

The theories of Weiss, Kunz and others,¹⁰ in an effort to account for deviations from Curie's law, consider the mutual action of the molecules or ions. These theories yield an expression $X = c/(T - \Theta)$ for the variation of susceptibility with temperature, where Θ is interpreted as a measure of the molecular field, which may be either positive or negative.

Williams'¹¹ work on neodymium oxide shows that the temperature variation may be expressed by $X = c/(T - \Theta)$ where $\Theta = -44^\circ$. The

⁸ Foex, *Trans. Am. Electrochem. Soc.*, 55, 97 (1929).

⁹ St. Meyer, *Physik. Z.*, 26, 51 (1925).

¹⁰ Weiss, *J. phys. Radium*, VI, 5, 129 (1924); Kunz, *Phys. Rev.*, 6, 113 (1915).

¹¹ Williams, *ibid.*, 12, 158 (1918).

variation in the susceptibility of neodymium nitrate found here could be accounted for by an increase of ten units (degrees C.) in Θ , the molecular field being considered negative. Over the limited temperature range available it would scarcely be possible to detect such a change in Θ directly, with the experimental apparatus described.

In the case of gadolinium sulfate, as is well known, Θ is practically zero, and it might be argued by analogy that, in view of the close chemical relationship between gadolinium and neodymium, the introduction of the molecular field in the case of the latter is artificial; but the author found almost no absorption spectra shift in the case of gadolinium solutions. The explanation is, perhaps, not that the gadolinium sulfate has no molecular field, but that its more stable electron structure is less sensitive to external influence.

The nature of the molecular field remains much in doubt. As stated by Stoner¹² "... the conclusion which may be drawn is that the molecular field cannot be interpreted as being simply either magnetic or electrostatic." However, "... that there are strong forces of some kind, whose effects are similar to those of magnetic fields, is undoubted."

While the work on nitrogen-oxygen mixtures tends to show that the molecular field is a function of the concentration of the magnetic molecule, the situation in such mixtures must be very different from that in the solution of an electrolyte.

Certain small temperature shifts in the absorption spectrum of gadolinium chloride are interpreted by Freed and Spedding¹³ as being due to a decrease in difference between the two energy levels involved, under the influence of the electric field of the neighboring negative ions. The same argument applies to the absorption shifts of neodymium previously reported by the author.

Now Fajans¹⁴ interprets an increase of refraction with concentration as resulting from the deformation of the cation owing to the approach of the negative field of the anion. While there is, of course, the possibility that the observed absorption and refraction changes take place by an entirely different mechanism than the magnetic change, still it is natural to try to relate them.

It has already been suggested by Cabrera and Duperier¹⁵ that the molecular field in the case of crystalline paramagnetic substances may be identified with the "deformation" of Fajans. They say, "It is evident that, in general, we can attribute the constant Θ to a deformation of the outer electron layer of the paramagnetic atom, under the action of the

¹² Stoner, "Magnetism and Atomic Structure," Methuen, London, 1926.

¹³ Freed and Spedding, *Phys. Rev.*, **34**, 945 (1929).

¹⁴ Fajans, *Trans. Faraday Soc.*, **23**, 357 (1927), *et seq.*

¹⁵ Cabrera and Duperier, *J. phys. Radium*, VI, 6, 121 (1925).

other atoms combined chemically with it." There seems no reason, then, why the shift of absorption bands should not be produced by the same mechanism. Some information as to the nature of the molecular field could be gained by measurements on the susceptibility of neodymium salts diluted with the isomorphic salts of the diamagnetic rare earth lanthanum.

The author wishes to thank Dr. Charles P. Smyth for his interest and advice in this work. He is also indebted to Dr. B. S. Hopkins, of the University of Illinois, for the use of several hundred grams of pure neodymium oxide.

Summary

The magnetic susceptibility of neodymium nitrate in aqueous solution has been found to decrease with increasing concentration. This behavior is discussed in connection with changes in absorption spectrum and refraction previously reported by the author, and with reference to Fajans' theory of the deformation of electron shells.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

OBSERVATIONS ON THE RARE EARTHS. XXXVII. ELECTROLYTIC PREPARATION OF RARE EARTH AMALGAMS. 1. PREPARATION OF AMALGAMS OF LANTHANUM AND NEODYMIUM¹

BY L. F. AUDRIETH, E. E. JUUKOLA AND R. E. MEINTS, WITH B. S. HOPKINS

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In line with a series of investigations² which are being carried out in this Laboratory involving the use of non-aqueous solvents for the electrodeposition of metals, preliminary experiments have been performed in an effort to plate the metals of the rare earth family from solutions of their salts in various organic and inorganic solvents, but with no marked success. That such a suggestion is not new is evident from the researches of Matignon,³ who prepared anhydrous salts of many of the rare earth elements and investigated their solubilities in various non-aqueous solvents. In connection with these studies he says, "If a solvent could be found in which salts (of the rare earth metals) ionized it would be easy to isolate the metals by simple electrolysis after the manner of Kahlenberg." Matignon had

¹ This paper was presented before the Division of Physical and Inorganic Chemistry at the Indianapolis meeting of the American Chemical Society, April, 1931.

² For earlier papers of this series see Yntema and Audrieth, *THIS JOURNAL*, **52**, 2693 (1930); Audrieth and Yntema, *J. Phys. Chem.*, **34**, 1903 (1930); Audrieth and Nelson, *Chem. Rev.*, **8**, 335 (1931).

³ Matignon, *Ann. chim. phys.*, **VIII**, **8**, 267 (1906).