Fig. 3.

and 50 cc. of distilled water contained in a 250-cc. separatory funnel. The acid obtained by the above procedure was titrated with approximately 0.1 N sodium hydroxide solution, using methyl red indicator. All corrections due to reagents were found to be negligible. This method was very satisfactory except for isopropyl sulfide, which, according to Sampey, Slagle and Reid, gives slightly high results.

Summary

Specific gravities at $0°/4°$, $20°/4°$ and $25°/4°$ were determined for pure samples of ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-amyl and isoamyl sulfides. Refractive indices at 20 and 25° for the D sodium line were also determined for the same sulfides. From these values the molecular refraction values were calculated.

from a dropping bottle to 50 cc. of c. p. benzene

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Residual Paramagnetism in Compounds of Lanthanum[1]

BY ROBERT B. HALLER AND P. W. SELWOOD[2]

Some years ago one of the writers[3] pointed out an apparent anomaly in the magnetic susceptibility of lanthanum oxide. On theoretical grounds the lanthanum ion may be expected to be diamagnetic with no temperature coefficient of susceptibility. Nevertheless, the purest lanthanum oxide contained a small paramagnetic residue which became evident as the temperature was lowered. Further study of this problem is desirable because magnetic susceptibility is often used as a criterion of purity of lanthanum compounds, and because the small but measurable ortho–para hydrogen conversion on pure lanthanum oxide surfaces[4] is inexplicable unless some paramagnetism on or in the compound is postulated.

Experimental Part

Preparation of Materials.—The lanthanum used in this work had been prepared under the direction of Dr. Frank

T. Gucker, of Northwestern University, through whose courtesy the authors received a sample sufficient for their purposes. This material had been separated from other rare earths by prolonged fractional crystallization of the ammonium double nitrates. Cerium had been removed by alkaline oxidation with potassium permanganate. The lanthanum had been precipitated repeatedly as oxalate, and then as sulfate enneahydrate.[3]

The present authors reprecipitated the lanthanum as hydrated sulfate. The material now showed no selective absorption in the visible through a 10-cm. layer of saturated nitrate solution in water, indicating the absence of praseodymium and neodymium. The familiar peroxide test for cerium also was negative. Careful qualitative tests failed to reveal the presence of any impurity.

Part of this material was reserved for susceptibility measurements. The remainder was divided into two portions, one of which was converted directly into oxide by ignition at 1000° for sixty hours. The sulfate decomposes slowly but the final sample of oxide obtained gave no cloudiness when dissolved in nitric acid and treated with barium chloride.

The remaining sulfate hydrate was dissolved in a large volume of water at room temperature and was precipitated as oxalate by addition of oxalic acid. The oxalic acid had been purified by repeated recrystallization from redistilled hydrochloric acid followed by recrystallization from distilled water. Part of the lanthanum oxalate was converted to oxide by ignition for one hour at 920°.

Care was taken throughout to prevent the oxide samples

(1) Presented in part under the title "Magnetic Measurements in Rare Earth Chemistry" at the Second Annual Symposium of the Division of Physical and Inorganic Chemistry on the Less Familiar Elements, Cleveland, Ohio, December 27, 28, and 29, 1937.

(2) The authors are indebted to the National Research Council for funds for the construction of a magnet, and to the Penrose Fund of the American Philosophical Society for funds for research assistance.

(3) Selwood, THIS JOURNAL, 55, 3161 (1933).

(4) Taylor and Diamond, ibid., 57, 1251 (1935).

from changing to carbonate by absorption of carbon dioxide from the air.

Measurements of magnetic susceptibility were then conducted on the four samples prepared, namely: the sulfate enneahydrate $La_2(SO_4)_3 \cdot 9H_2O$, the oxalate $La_2(C_2O_4)_3 \cdot 10H_2O$, the oxide derived directly from the sulfate La_2O_3(sulf.), and the oxide derived from the sulfate by way of the oxalate La_2O_3(oxal.).

Magnetic Measurements.—The magnetic susceptibilities were measured by means of the Gouy balance, which has often been described elsewhere.[5-7] The only unusual features of the apparatus were (1) the use of a microbalance to measure the changes in apparent weight of the sample, (2) the field strength control, and (3) the temperature control. The field was controlled as follows: the current entering the magnet was passed through a standard 0.01 ohm resistance from which leads ran to a potentiometer. The potentiometer was connected to a sensitive galvanometer from the mirror of which a beam of light was reflected into two photoelectric cells. The cell response after amplification, operated a reversible motor connected to a rheostat, which in turn controlled the current in the field coils of the d. c. generator supplying the magnet. This device proved satisfactory for maintaining the magnet field strength constant over a period of an hour or more. The maximum fields used were about 5000 gausses. In practice it was found best to make measurements with the current through the magnet set at 12.0, 12.2, 12.4, 12.6, 12.8, and 13.0 amperes. The results obtained were then plotted against current in order to get an accurate average at 12.5 amperes. This procedure also served as an automatic check against ferro-magnetic impurities in the samples.

Measurements were made at the temperatures 20 and $-150°$. In order to maintain the lower temperature the sample was inserted in a hole in a large (7 kg.) block of lead. The lead block was shaped to fit a tubulated Dewar flask, and was drilled to admit liquid air for cooling purposes. When this device was cooled to $-150°$ it warmed up at the rate of 0.2° per minute. After a little practice it was found possible, by careful injections of liquid air, to maintain the temperature within $\pm 0.05°$. The temperature of the lead block was measured by means of a calibrated thermocouple. The temperature of the block was shown to be identical with that of the sample provided sufficient time, about one hour, was allowed for the attainment of equilibrium. The temperatures are believed to be accurate to $\pm 0.05°$. This degree of temperature control was not necessary because of any high temperature coefficient of magnetic susceptibility, but rather because of the buoyancy effect of the surrounding atmosphere (N_2) which varied sharply with changing temperature.

The samples were measured in the familiar double-ended Pyrex tube. The tube capacity was 1.3 cc. and the length of each end 14 cm. The apparatus was calibrated with distilled, freshly boiled water, the specific susceptibility of which was taken as -0.720×10^{-6}. The magnetic measurements are believed to be accurate to ± 0.002

(5) Stoner, "Magnetism and Matter," Methuen, London, 1934.

(6) Bhatnagar and Mathur, "Physical Principles and Applications of Magnetochemistry," The Macmillan Co., London, 1935.

(7) Klemm, "Magnetochemie," Akademische Verlagsgesellschaft m, b, H., Leipzig, 1936,

$\times 10^{-6}$ units of susceptibility. The principal error arises through uneven packing of the material in the sample tube. The measurements on any one sample are believed to be comparable to $\pm 0.0002 \times 10^{-6}$ because it was possible to make measurements at different temperatures without disturbing the material in the sample tube. This high degree of accuracy was achieved through use of a balance reading to 1 microgram, and through careful control of the field strength and temperature.

Results

The results obtained are summarized in Table I which gives the specific (or gram) susceptibility at the two temperatures. The values reported

TABLE I

	$La_2(SO_4)_3 \cdot 9H_2O$	$La_2(C_2O_4)_3 \cdot 10H_2O$	La_2O_3 (sulf.)	La_2O_3 (oxal.)
$\chi_{20} \times 10^6$	−0.3617	−0.3064	−0.1848	−0.1406
$\chi_{-150} \times 10^6$	− .3454	− .2582	− .1561	− .1217

for sulfate and oxalate are not very different from those reported by other writers. The fact that the susceptibility of the oxides is much smaller than the value (-0.40×10^6) given elsewhere[8] is not regarded as being significant. The writers are convinced that the magnetic susceptibility of lanthanum oxide is markedly dependent on the method of preparation. It is sufficient for the present purposes that every sample of the oxide prepared in the *same* way gave the same susceptibility.

The above results are seen to follow the relationship $\chi = A + (C/T)$ where A and C are constants and T the absolute temperature. In this case A is negative, C positive. This is precisely the situation to be expected if the diamagnetic compound contained a small amount of paramagnetic impurity. Interpretation of the data is therefore facilitated by calculating the amount of diamagnetism and of paramagnetism actually present in the substances, assuming, of course, the validity of Wiedemann's law. In Table II A is the diamagnetic part of the susceptibility and B the paramagnetic part at 20°. It is evident that $B = C/293$, and that $A + B = \chi_{20}$.

TABLE II

	$La_2(SO_4)_3 \cdot 9H_2O$	$La_2(C_2O_4)_3 \cdot 10H_2O$	La_2O_3 (sulf.)	La_2O_3 (oxal.)
$A \times 10^6$	−0.3735	−0.3372	−0.2055	−0.1543
$B \times 10^6$	+ .0118	.0308	.0207	.0137

Discussion of Results

Various interpretations of the above data suggest themselves. These are (1) the presence of paramagnetic impurities, (2) the paramagnetic

(8) "International Critical Tables," Vol. VI, p. 359.

contribution of the nuclear spins, (3) the partial reduction of La^{+++} to a paramagnetic ion, and (4) the existence of "surface" paramagnetism.

The presence of paramagnetic impurities is the most obvious explanation for the results obtained. The writers do not, however, believe it to be the true explanation. The most likely impurities in any rare earth sample are other rare earths. In the case of lanthanum the nearest neighbors, and the last to be removed, are cerium and praseodymium. These elements form strongly paramagnetic compounds. It is therefore necessary to calculate what percentage of each of these could give rise to the observed effects. Cerium may be present as Ce^{+++} or Ce^{++++}, but the quadrivalent cerium ion contains no 4f electron and is diamagnetic. It is true that ceric oxide shows a small positive susceptibility, but this is independent of temperature and could not have contributed to the observed effects. On the other hand, the specific susceptibility of cerous oxide, Ce$_2$O$_3$, may be estimated from the various published data[5,8] to be about 8 × 10^{-6}. The amount of cerous oxide impurity in the lanthanum oxide would therefore have to be at least 0.26%. However, the chemical test for cerium using hydrogen peroxide and ammonium hydroxide is believed to be sensitive to 1 part per 100,000. This test was negative. The presence of cerium as an explanation of the results with lanthanum is therefore ruled out.

Praseodymium may exist in two oxidation states. In the quadrivalent oxide it is isoelectronic with cerous cerium. The oxide PrO$_2$ does not appear to have been measured, but its susceptibility is probably about the same as that of Ce$_2$O$_3$. Praseodymium in the higher valence state would certainly have to be present to the extent of over 0.2% in order to give rise to the observed effect. Apart from the negative spectroscopic evidence it is probable that such a concentration of praseodymium dioxide would impart a dark color to the lanthanum oxide. No such color was observed. The susceptibility of praseodymium sesquioxide is considerably larger than that of the dioxide. Nevertheless, over 0.1% of Pr$_2$O$_3$ would be required to give rise to the observed effects. This too is much higher than the limit allowed by the negative spectroscopic evidence. The absence of praseodymium automatically implies the absence of neodymium or of any other member of the rare earth family. This is

true because the serial separation order is identical with the atomic number in an ammonium double nitrate fractionation series.

Other impurities, especially iron, were eliminated by chemical tests. Sodium, calcium, and magnesium were doubtless present in small quantities, but these are all diamagnetic.

Another possible impurity is oxygen from the air, either adsorbed on, or filling the interstices between, the particles of rare earth compound. No information is at present available as to the magnetic properties of adsorbed oxygen, but assuming that they are the same as those of gaseous oxygen, a simple calculation shows that the sample tube would have had to be over half full of air in order to give rise to the observed effects. While it is by no means impossible that a gram of lanthanum oxide may adsorb a cubic centimeter of air, still it is quite unlikely that the lanthanum oxalate would adsorb even more oxygen than the oxide. The presence of molecular oxygen is therefore regarded as an improbable source of the observed results.

It is well known that nuclear spin contributes toward the paramagnetism of an atom, but the nuclear spin contribution is very small,[9] amounting to about 10^{-9} susceptibility units per gram molecule at room temperature, or less than 10^{-11} units per gram in the present measurements. Such small susceptibilities could not be detected with the authors' apparatus.

Another possibility is the partial reduction of lanthanum from La^{+++} to La^{++}. So far as the writers know, there has never been any evidence to show that lanthanum is multivalent. Nevertheless, there is no very obvious reason why the structure 4f5s^{2}5p^6 should not be nearly as stable for lanthanum as it is for cerium. If the La^{++} ion exists it is isoelectronic with Ce^{+++} and should have about the same susceptibility. About 0.26% of reduced lanthanum would therefore be sufficient to account for the observed effect. The writers are inclined to doubt this explanation because the lanthanum oxide prepared in an oxidizing atmosphere (ignition of the sulfate) has a somewhat higher paramagnetic component than has the oxide prepared in a reducing atmosphere (ignition of the oxalate).

A final explanation, and one which the writers are inclined to favor, is the possible existence of

(9) Van Vleck, "Electric and Magnetic Susceptibilities," Oxford Univ. Press, New York, 1932.

"surface" paramagnetism. A number of writers[4] have postulated the existence of a paramagnetic layer on the surface of many if not all solids. This postulate has been introduced to account for the small but measurable ortho–para hydrogen conversion on solids ordinarily considered to be diamagnetic. Although small, such conversion is greater than can be accounted for by the influence of nuclear spins. The reason why the surface layer of atoms should be paramagnetic has never been explained, nor has any direct relationship been reported between the surface of a powder and its supposed paramagnetism. The present experiments establish that relationship in a qualitative way because the crystalline lanthanum sulfate has obviously much less surface than either the oxides or the oxalate. The sulfate shows the smallest temperature coefficient of susceptibility. A possible mechanism for the effect may be the dropping of an electron back into the 4f shell in the surface atoms only. It seems not impossible that the high electric dissymmetry of the surface could achieve what ordinary chemical reducing agents cannot. A somewhat parallel effect has been observed[10] in the case of zinc oxide. This compound has a slight temperature coefficient of susceptibility which disappears on sintering, that is, reducing the surface. The implication is clear,

therefore, that the effect described here is associated with transition group elements, but is actually observable only with the diamagnetic elements at the beginning or end of a transition group. This will be true because the "surface" paramagnetism is at best small, and will be completely masked by the large normal paramagnetism of those elements actually members of a transition group. The effect should be shown by compounds of the following elements, besides those already named: cadmium, mercury, scandium, yttrium, and lutecium. Sufficiently accurate data on these elements are not yet available for an adequate test of this prediction.

Summary

Accurate measurements of magnetic susceptibility at 20 and −150° have been made on the compounds $La_2(SO_4)_3 \cdot 9H_2O$, $La_2(C_2O_4)_3 \cdot 10H_2O$, and La_2O_3, the last-named being prepared in two different ways. A slight residual paramagnetism was observed in all cases. The possible causes of this phenomenon are examined. It is suggested that this work constitutes direct observation of the so-called "surface" paramagnetism which has been postulated to explain the small ortho–para hydrogen conversion on supposedly diamagnetic surfaces.

(10) Turkevich and Selwood, unpublished.

Arsonium Compounds. II[1,2]

BY F. F. BLICKE, HOBART H. WILLARD AND J. T. TARAS

Some time ago the discovery was made by one of us (H. H. W.) that tetraphenylarsonium chloride[3] is a unique and very valuable analytical reagent. It serves for the quantitative precipitation of perrhenate, periodate, perchlorate, permanganate and other anions. As far as the authors are aware tetraphenylarsonium permanganate is the only insoluble permanganate known. Tetraphenylarsonium chloride is useful also in the determination of zinc, cadmium, mercury, gold, platinum and other metals.[4,5]

(1) Paper I, Blicke and Cataline, THIS JOURNAL, 60, 423 (1938).

(2) This investigation was made possible by a grant from the Faculty Research Fund of the University of Michigan.

(3) Blicke and Monroe, THIS JOURNAL, 57, 722 (1935).

(4) A full account of the analytical applications of the arsonium chloride will be published soon by Willard and Smith.

(5) Other organic arsenicals which have found application in

The preparation of tetraphenylarsonium chloride,[6] while not especially difficult, is more labori-

analytical chemistry are arsonic acids. Thus, phenylarsonic acid has been used for the determination of zirconium and thorium by Rice, Fogg and James [THIS JOURNAL, 48, 895 (1926)]; for zirconium by Klinger and Schliessmann [Arch. Eisenhüttenw., 7, 113 (1933)] and for tin by Knapper, Craig and Chandlee [THIS JOURNAL, 55, 3945 (1933)]. Tougarinoff [Bull. soc. chim. Belg., 45, 542 (1936)] used nitrophenylarsonic acid for the estimation of tin. Iron has been determined with the aid of p-n-butylphenylarsonic acid by Craig and Chandlee [THIS JOURNAL, 56, 1278 (1934)]; Arnold and Chandlee [ibid., 57, 8 (1935)], as well as Geist and Chandlee [Ind. Eng. Chem., Anal. Ed., 9, 169 (1937)], have used n-propylarsonic acid for zirconium; see also Chandlee, THIS JOURNAL, 57, 591 (1935). Recently the use of p-hydroxyphenylarsonic acid as a reagent for titanium and zirconium has been described by Simpson and Chandlee [Ind. Eng. Chem., Anal. Ed., 10, 642 (1938)]. Feigl, Krumholz and Rajmann [Mikrochemie, 9, 395 (1931)] have used p-dimethylaminoazophenylarsonic acid for the detection of zirconium and Bullard [J. Chem. Education, 14, 312 (1937)] described the use of phenylarsonic acid in the qualitative test for tin.

(6) This reagent can be purchased from Merck and Company.