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# Magnetic properties of some intra-rare earth alloys

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MAGNETIC PROPERTIES OF SOME INTRA-RARE EARTH ALLOYS

by

Paul Edward Roughan

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1962

## TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. LITERATURE SURVEY	14
A. Magnetic Properties of Rare Earth Ions-- Theory and Experiment	14
B. Magnetic Properties of Rare Earth Metals	16
C. Intra-Rare Earth Alloy Systems and Their Magnetic Properties	21
III. EXPERIMENTAL PROCEDURE	28
A. The Gouy Method for the Measurement of Paramagnetic Susceptibilities	29
1. Theory	29
2. Apparatus	32
B. Susceptibility Measurements by the Mutual Inductance Bridge Method	41
1. Theory	41
2. Experimental	43
C. Preparation of Alloys	46
IV. RESULTS	51
A. X-ray Diffraction Data	51
B. Gouy Data	52
C. Mutual Inductance Data	58
V. DISCUSSION	94
VI. BIBLIOGRAPHY	104
VII. ACKNOWLEDGEMENTS	109

## I. INTRODUCTION

The magnetic properties of a substance can be described by stating which of the five known types of magnetic phenomena the substance exhibits. The five types are diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism and ferrimagnetism. Before discussing the origins and characteristics of these phenomena, it will prove helpful to define some terms which will be used throughout this work.

If a substance is placed in a magnetic field of strength  $H$ , then  $B$ , the magnetic induction, or the total number of lines of magnetic force passing through unit area of substance, is given by

$$B = H + 4\pi I$$

The quantity  $I$  is called the intensity of magnetization, and  $I/H = k$  is the magnetic susceptibility per unit volume. The permeability,  $\mu$ , can be defined as the ratio of  $B$  to  $H$ , and is taken as unity in vacuo. With these definitions in mind, we can proceed to discuss the various types of magnetism listed above.

Diamagnetism, since it is a universal property of matter, will be discussed first. When a magnetic field is being established in a substance, its time rate of change induces electromotive forces in the atoms, and these emfs in

turn build up circulating currents within the atoms. Since there is no resistance to these currents, they persist as long as the magnetic field continues, and give rise to magnetic moments. By Lenz's law, these moments are in opposition to the external field; thus the diamagnetic effect results in a permeability less than unity, i.e., the intensity of magnetization produced in the substance is slightly smaller than that produced in a vacuum by the same external field. Physically, this situation can be pictured by imagining the magnetic lines of force to be bent slightly away from the boundaries of a diamagnetic substance. Using classical and quantum mechanical methods, respectively, Langevin (1905) and Van Vleck (1932) arrived at the same expression for the atomic diamagnetic susceptibility:

$$\chi_A = -(Ne^2/6mc^2) \Sigma \bar{r}^2$$

Here,  $N$  is Avogadro's number,  $e$  and  $m$  are the electronic charge and mass, respectively,  $c$  is the velocity of light, and  $\bar{r}^2$  is the mean square radius of the electronic orbit. Thus, diamagnetism depends only on the effective radius of the electronic orbits, and is therefore independent of temperature and of field strength.

Paramagnetism is exhibited by substances whose atoms possess permanent magnetic moments; generally the existence

of such a moment is due to the presence of one or more unpaired electrons in the atom. This moment arises from two sources: the orbital magnetic moment, produced by the motion of the electrons around the nucleus, and the spin magnetic moment, an inherent property of the electron due to its rotation about its own axis. In the absence of a magnetic field, these moments can be oriented in any direction in space. When a field is applied, however, spatial quantization allows only certain orientations, characterized by the angular momentum along the field axis equal to an integral or half-integral multiple of  $h/2\pi$ . Thus definite energy levels arise, since the magnetic energy is obtained from the product of field strength and the component of magnetic moment along the field. At high temperatures, all of the allowed orientations would be equally likely, but at lower temperatures, the Boltzmann factor, which indicates that the probability of finding an atom with energy  $E$  is proportional to  $\exp(-E/kT)$ , shows that those orientations with low energy (magnetic moment directed along the field) are more likely than those with high energy (magnetic moment oriented in opposition to the field). Thus one is led to assume an average moment, proportional to the magnetic field, and inversely proportional to the absolute temperature. A paramagnetic substance, then, exhibits a permeability greater than unity, and a susceptibility which is temperature dependent, although independent

of field strength.

The three other known types of magnetism are all different aspects of the same phenomenon. The major difference between ferromagnetism, antiferromagnetism and ferrimagnetism on the one hand, and paramagnetism and diamagnetism on the other, is that the former are group effects, while the latter are atomic or molecular in nature. Ferromagnetism is difficult to define simply and precisely, and for this reason an operative definition is usually employed. The susceptibility of a ferromagnetic substance is extremely high at low fields, orders of magnitude larger than that of the most highly paramagnetic substances. The specific magnetization of a ferromagnetic material is a function of field, up to a certain field at which the substance is said to be saturated; for most materials, this field is easily attainable. Many ferromagnetic substances exhibit the phenomena of hysteresis and of residual magnetism.

Until Heisenberg (1928) first applied the methods of quantum mechanics to the problem, very little was known about the origins of ferromagnetism; even today, despite the wealth of data and experience available, Bozorth (1960) comes uncomfortably close to the truth when he states:

It may be said facetiously that in the iron group of elements, iron, cobalt, and nickel, much less is understood (concerning their ferromagnetism) now than fifteen years ago.



Without becoming involved in the complex ramifications of current theories, one can give a simplified picture of the origins of ferromagnetism in the following manner:

As implied above, a paramagnetic material can be pictured as one in which there is very little or no coupling between the individual atomic magnets. The atomic moments are oriented randomly, and extremely high fields, and/or very low temperatures are required for alignment. If, however, there exists some sort of strong coupling between these atomic magnets, the thermodynamically stable state of the material may prove to be that in which all of the moments are aligned in a parallel manner. When this occurs, the material is said to be ferromagnetic. The fact that the bulk material may show no sign of being strongly magnetic is explained by the existence of ferromagnetic "domains" in the material; in any one domain, the moments are all parallel, although the domains themselves may be arranged in such a fashion as to effectively cancel each other, and thereby reduce the net magnetization considerably.

In an antiferromagnetic material, the coupling between the atomic magnets is such as to align the moments of nearest neighbor atoms in an antiparallel fashion. The net moment of the substance is greatly reduced, and the susceptibility is of the same order of magnitude as that of a paramagnetic substance. In contrast to the paramagnetic case, however,

the susceptibility in the antiferromagnetic region is usually independent of temperature.

Ferrimagnetism can occur only in compounds, since the existence of moments of different magnitude is necessary to produce this type of magnetism. The nearest neighbor coupling in this case is antiferromagnetic (moments antiparallel), but it occurs between unlike atoms, producing a resultant magnetic moment. Broadly speaking, one can classify ferrimagnetic materials into two categories: one type, of which zinc ferrite,  $\text{ZnFe}_2\text{O}_4$ , is an example, has a susceptibility comparable to that of paramagnetic substances, while the other, e.g.,  $\text{NiFe}_2\text{O}_4$ , has values of the magnetic moment per unit volume similar to those of ferromagnetics, which are many orders of magnitude greater than the values exhibited by paramagnetic substances.

At high enough temperatures, all three types of alignment disappear, and the material becomes paramagnetic. This, of course, is due to the fact that the thermal energy is sufficient to overcome the tendency toward alignment, and the moments again become randomly oriented. The temperature at which this transition occurs is known as the Curie point in the case of a ferro- or ferrimagnetic material, and the Néel point in an antiferromagnetic material. It should be noted, however, that the susceptibility of a ferrimagnetic substance, at temperatures near the Curie point, does not

follow the Curie-Weiss law. Instead of a straight line, as in the case of an antiferro- or ferromagnetic material, the curve of  $1/\chi$  vs.  $T$  for a ferrimagnet is an hyperbola, with its concavity towards the temperature axis. Well above the Curie point, the susceptibility obeys a Curie-Weiss law.

As will be noted, the operative word in the above discussions of magnetic ordering is the word "coupling". The nature of this coupling will be explored in detail in a later section of this work.

With the foregoing discussion in mind, one can appreciate the fact that a wealth of information about a given substance can be obtained by an investigation of the magnetic properties of the substance. For the investigator who desires to learn about magnetic phenomena in nature, there is probably no other group of elements more fruitful for study than the rare earth metals.\* Every type of magnetism known is exhibited by these elements and their compounds. The metals scandium, yttrium, lanthanum, ytterbium and lutetium are essentially diamagnetic, although one does observe a small, temperature independent paramagnetism associated with the conduction electrons in these metals. All of the other

---

\*In this work, the author includes as rare earth metals scandium, yttrium, and the elements of atomic numbers 57 through 71, in accordance with the nomenclature recommended by the International Union of Pure and Applied Chemistry (1960).

rare earths, cerium through thulium, are paramagnetic at high temperatures, and exhibit transitions to antiferromagnetism and/or ferromagnetism at low temperatures. The well-known rare earth garnets, which usually are iron or nickel oxides, "doped" with a rare earth, are ferrimagnetic.

As a result of the many investigations that have been carried out on the magnetic properties of the rare earth metals, the following model for their magnetic behavior has emerged: in the paramagnetic region, the metals can be pictured as consisting of non-interacting tripositive ions, with the possible exception of europium; the paramagnetic behavior is very well explained by attributing the paramagnetism to the electrons in the 4f subshell, which is built up as one proceeds across the series from lanthanum (no 4f electrons) to lutetium (fourteen 4f electrons). According to this scheme, europium and ytterbium should have six and thirteen 4f electrons, respectively. It has been found, however, that there is a marked tendency for these elements to assume the more stable configurations  $4f^7$ , in which the shell is half-filled, and  $4f^{14}$ , in which the shell is completely filled. These metals, then, behave as though they were composed of dipositive ions. In the case of europium, its susceptibility is similar to that of gadolinium (although in general the metal europium is not well-behaved magnetically), while ytterbium is diamagnetic, since there are

no unpaired electrons in the  $4f^{14}$  configuration.

Since the  $4f$  electrons are situated deeply within the atom, and hence are neither directly involved in bonding nor subject to perturbations from neighboring atoms, the full contribution of their orbital magnetic moment is realized. This is in contrast to the situation which applies in those transition metal periods which are built up through the addition of  $d$  electrons; here the electrons responsible for paramagnetism are not localized on the atom, and are affected to a great extent by the atomic environment. The orbital contribution of these electrons can range from essentially zero all the way up to their full theoretical value, depending on the extent of the  $d$  electron interactions.

As stated above, some sort of strong coupling between the atomic magnets is necessary to produce magnetic ordering. One can qualitatively see how such coupling can occur in those transition metals like iron, cobalt and nickel, where the  $d$  electrons are able to interact with those of neighboring atoms. For the rare earth metals, however, such a direct interaction is not possible, and an indirect interaction has been postulated as the mechanism for the magnetic ordering which occurs in these metals. This interaction proceeds via the conduction electrons, whose spins become polarized by the  $4f$  electrons; these spin-polarized conduction electrons, which are free to move throughout the lattice, are able to transfer

this polarization to the 4f electrons of neighboring atoms, and in this manner, the spins become aligned and magnetic ordering is produced.

Investigations designed to shed more light on the nature of the conduction-electron magnetic-ion interaction in the rare earths appear to be the next logical step in the progress of research into the magnetic properties of these metals. One approach to this problem which should prove fruitful involves the measurement of the magnetic properties of intra-rare earth alloys, in order to determine whether the same ordering mechanism operates between two rare earths of different magnetic moments. Since such an approach is explored in the present work, it should prove helpful to give a brief discussion of the alloying behavior of one rare earth metal with another.

The Hume-Rothery criteria for predicting alloy behavior include four properties of the alloy constituents: atomic sizes, relative valencies, electronegativities, and crystal structures. When the atomic sizes and crystal structures are similar, solid solution should occur; if the electronegativities are quite different, compound formation is expected, and a metal of lower valency is more likely to dissolve one of higher valency than vice versa. In the rare earth series, the first three of these properties are quite similar, however, there exist several different crystal

structures among these metals. At room temperature, scandium, yttrium and the elements from gadolinium through lutetium are hexagonal close-packed, with the normal stacking plan, pictured as ABABABAB etc., and c/a ratios of about 1.57; lanthanum, praseodymium and neodymium are also hexagonal, but with a double c-axis. This arrangement corresponds to the stacking plan ABAC..ABAC etc. and leads to c/a ratios of about 3.1 for these metals. Cerium and ytterbium are face-centered cubic, while europium is body-centered cubic and samarium is rhombohedral. Cerium, moreover, undergoes an allotropic transformation, at 263°K., to a structure isomorphous with lanthanum, praseodymium and neodymium; Gschneidner and Smoluchowski (1961) have found that this allotrope can be characterized by a valence of 3.62 at 116°K., an observation which would lead one to assume the presence of both tripositive and tetrapositive cerium ions.

It will be shown in a later section that, in addition to exhibiting different crystal structures, it has been found that the so-called "light" rare earths (lanthanum through neodymium) have different magnetic properties than the "heavy" rare earths (scandium, yttrium, and gadolinium through lutetium), at low temperatures. It thus becomes of interest, first to examine the alloying behavior of a light rare earth with a heavy, and secondly, to examine the physical properties of such alloys. Valletta et al. (1962) have shown, in the

systems cerium-yttrium, praseodymium-yttrium, neodymium-yttrium, lanthanum-yttrium, lanthanum-gadolinium and neodymium-thulium, the existence of a phase, usually occurring at compositions close to 50 atomic percent, which is stable over a composition range of about 3-4 atomic percent, and has the rather remarkable characteristic of displaying the crystal structure of samarium, i.e., rhombohedral, with approximately the same lattice constants as samarium metal. This phase will be referred to as the  $\delta$  phase throughout this work. It thus appears that the unusual (for a metal) crystal structure exhibited by samarium is actually a sort of transition structure between the light and heavy rare earths, since the atomic number of samarium places it at about the dividing line between the light and heavy members of the rare earth series.

In this work, the magnetic properties of four of these  $\delta$  phase alloys, lanthanum-gadolinium, cerium-yttrium, neodymium-yttrium and neodymium-thulium, will be investigated, in order to determine what effect, if any, the formation of this structure has on the magnetic properties of the alloy. It will be noted that, in the lanthanum-gadolinium binary alloy system, the light rare earth is diamagnetic, and the heavy is paramagnetic; in the neodymium-yttrium system, the reverse is true, while in the neodymium-thulium system, both constituents are paramagnetic. Thus all three different types



of  $\delta$  phases are investigated. The cerium-yttrium alloy was examined because of the low temperature allotropy of cerium; if any change took place in the valence of cerium, it was hoped that it would be apparent from the susceptibility data.

## II. LITERATURE SURVEY

A. Magnetic Properties of Rare Earth Ions--  
Theory and Experiment

The magnetic properties of the salts of the rare earths have been very thoroughly investigated by a large number of workers, and there are excellent reviews of the field available. Van Vleck (1932), Stoner (1934), Gorter (1932) and Cabrera (1939) have described the early work, and Selwood (1956) has summarized a large part of the more recent work. In general, it has been found that the paramagnetic susceptibilities of the rare earth ions follow the Curie-Weiss law:

$$\chi = \frac{C}{T - \theta}$$

where  $\chi$  is the mass susceptibility,  $C$  the Curie constant,  $T$  the absolute temperature, and  $\theta$  the Weiss constant. It is sometimes assumed that, when  $\theta$  is positive, it corresponds to a Curie temperature, and when it is negative, to a Néel temperature. However, the connection between the Weiss constant and theory is a tenuous one at best, and its use as a criterion of magnetic transitions is open to question. It would appear to be better to regard  $\theta$  as an experimental parameter, which arises from the fact that, as magnetic

measurements have become more precise, very few substances have been found which obey the simple Curie law,  $\chi = C/T$ .

The theory of the paramagnetic susceptibility of rare earth ions is largely due to the work of Hund (1925) and Van Vleck (1932). The latter developed the following expression for the susceptibility, which is obeyed by most of the rare earths:

$$\chi_M = \frac{N g^2 \beta^2 J(J+1)}{3kT} + N\alpha$$

Here,  $\chi_M$  is the susceptibility per mole,  $N$  is the Avogadro number,  $\beta$  is the magnetic moment of one Bohr magneton, and  $k$  is the Boltzmann constant. Following the usual spectral notation,  $J$  is the vector sum of  $L$  and  $S$ , the resultant orbital and spin moments, respectively;  $g$  is the Lande splitting factor, given by:

$$g = 1 + \frac{S(S+1) + J(J+1) - L(L+1)}{2J(J+1)}$$

The term  $N\alpha$  involves the temperature independent contribution of high frequency elements of the magnetic moment, and is usually small enough to be neglected, except in the special cases of europium and samarium. In these elements, and to a lesser extent in praseodymium and neodymium, the energy separation between  $J$  levels is of the order of  $kT$ , at ordinary

temperatures; thus, higher J levels can become populated, and contribute to the susceptibility. Van Vleck and Frank (1929) employed a more general theory to account for the discrepancies observed in the magnetic properties of these metals; the correct expression is as follows:

$$\chi_M = \frac{N \sum_J [(g_J^2 \beta^2 J(J+1)/3kt) + \alpha_J] (2J+1) \exp(-E_J/kT)}{\sum_J (2J+1) \exp(-E_J/kT)}$$

The sums are taken over all possible values of J, from  $J = |L-S|$  to  $J = L+S$ . The term in  $\alpha$  is given by:

$$\alpha_J = \frac{\beta^2}{6(2J+1)} \left[ \frac{F_{J+1}}{E_{J+1} - E_J} - \frac{F_J}{E_J - E_{J-1}} \right]$$

where

$$F_J = \frac{1}{J} \left[ (S+L+1)^2 - J^2 \right] \left[ J^2 - (S-L)^2 \right]$$

By means of the more general expressions outlined above, excellent agreement has been obtained between the experimental values and theory for all of the rare earth ions.

#### B. Magnetic Properties of Rare Earth Metals

The first thorough investigation of magnetism in the rare earth metals was carried out by Klemm and Bommer (1937)

who measured the susceptibility of all of the rare earth metals. Previously, lanthanum, cerium, neodymium and gadolinium had been investigated by Trombe (1934, 1935); later, la Blanchetais examined the magnetic properties of metallic cerium and praseodymium (1945, 1952). The ferromagnetism of gadolinium was discovered by Urbain et al. (1935), and the existence of ferromagnetism in dysprosium was later postulated by Klemm and Bommer (1937). This phenomenon was observed by Trombe (1945, 1953); in addition, the latter author also discovered the existence of an anti-ferromagnetic state in this metal.

At about this same period, Spedding and his co-workers at Iowa State University developed ion exchange methods for separating the rare earths (Spedding and Powell (1954)), and devised new techniques for producing the metals in higher purities than had previously been attained (Spedding and Daane (1954)). Since this time, the group at Iowa State University, under the direction of Spedding and Legvold, has carried on an extensive study of the magnetic properties of the pure rare earth metals. Out of these investigations have come several papers by Elliott et al., on gadolinium (1953), dysprosium (1954a), neodymium (1954b) and erbium (1955); in the latter work, the existence of ferromagnetism in erbium was established, and the existence of an antiferromagnetic state in this metal was proposed. The metals holmium and

thulium were investigated by Rhodes et al. (1958), and the data of these authors indicate that both elements undergo antiferromagnetic-ferromagnetic transitions at low temperatures, similar to dysprosium and erbium. Thoburn et al. (1958a) found that terbium metal also exhibited both antiferro- and ferromagnetism. More recently, magnetic measurements have been carried out on single crystals of some of the rare earth metals; Behrendt et al. have examined single crystals of neodymium (1957) and dysprosium (1958). In the former case, the authors found that neodymium became antiferromagnetic at very low temperatures (around  $4.2^{\circ}\text{K.}$ ). Other measurements on single crystals have now been completed on erbium (Green (1961)) and holmium (Strandburg (1961)).

The magnetic susceptibilities of lanthanum, cerium, praseodymium, neodymium and samarium have been measured, from  $1.3 - 300^{\circ}\text{K.}$ , by Lock (1957a). Low temperature anomalies, indicating the onset of antiferromagnetism, were found for cerium, neodymium and samarium. The same author (1957b) has investigated ytterbium metal over the same temperature range, and found only slight paramagnetism, indicating that this element is divalent in the metallic state. Leipfinger (1958) carried out magnetic susceptibility measurements on cerium, praseodymium, neodymium, samarium, terbium, holmium, dysprosium, thulium and ytterbium down to  $1.5^{\circ}\text{K.}$ , and his

data agree well with the results obtained by the other workers mentioned above. The magnetic properties of europium have been investigated, from 1.3 - 300°K., by Bozorth and Van Vleck (1960); the observed behavior is difficult to interpret, but the authors have proposed that the metal is divalent at high temperatures and trivalent at low temperatures. A Néel point was observed between 90 - 100°K., in agreement with the observations of La Blanchetais and Trombe (1956). Thulium metal has been examined magnetically by Davis and Bozorth (1960), and their results confirm the previous work of Rhodes et al. (1958), in which an antiferromagnetic-ferromagnetic transition was indicated.

The high temperature paramagnetic susceptibilities of metallic cerium (90 - 1057°K.) and neodymium (290 - 1000°K.) have been measured by Bates et al. (1955a,b). Very recently, a very thorough series of measurements have been carried out on the rare earth metals cerium through thulium, from 300 - 1500°K., by Araj's (1960a, Tm; 1960b, Sm), Araj's and Miller (1960a, Nd, Ho, Er), Araj's and Colvin (1960, Gd, Tb, Dy), Araj's et al. (1961, Pr), and Colvin et al. (1961, Ce, Eu). These authors have found that the paramagnetic behavior of all the metals studied except europium could be interpreted by using the tripositive ion model based on the localized 4f electron approximation, and the Van Vleck theory of paramagnetism. A small, temperature independent paramagnetic

susceptibility, of magnitude  $1 \times 10^{-6} \text{g}^{-1} \text{cm}^3$ , was found to be present, originating from the conduction electrons of these metals. The observations of these authors on the susceptibility of europium indicate that the tripositive model can only be applied below the Néel temperature ( $90^\circ\text{K}$ ). Above this temperature, the behavior is described by the  $\text{Eu}^{++}$  approximation, gradually approaching an  $\text{Eu}^+$  model at higher temperatures. The susceptibility of liquid europium indicates the presence of  $\text{Eu}^{++}$  ions.

Table 1 was compiled from the data given in the above papers on the magnetic properties of the rare earth metals, and also data on the electrical resistivities of these metals, reported by Alstad *et al.* (1961), Curry *et al.* (1960), and Colvin *et al.* (1960). This table lists the Néel points ( $T_N$ ) and Curie points ( $T_C$ ) in  $^\circ\text{K}$ ., for the pure metals.

Table 1. Magnetic transition temperatures of rare earth metals

Metal	$T_N$	$T_C$	Metal	$T_N$	$T_C$
Ce	12.5	-----	Gd	-----	291
Pr	-----	-----	Tb	229	219
Nd	7.5	-----	Dy	174	90
Sm	14.8	-----	Ho	127	19
Eu	90	-----	Er	80	20
			Tm	54.5	22



### C. Intra-Rare Earth Alloy Systems and Their Magnetic Properties

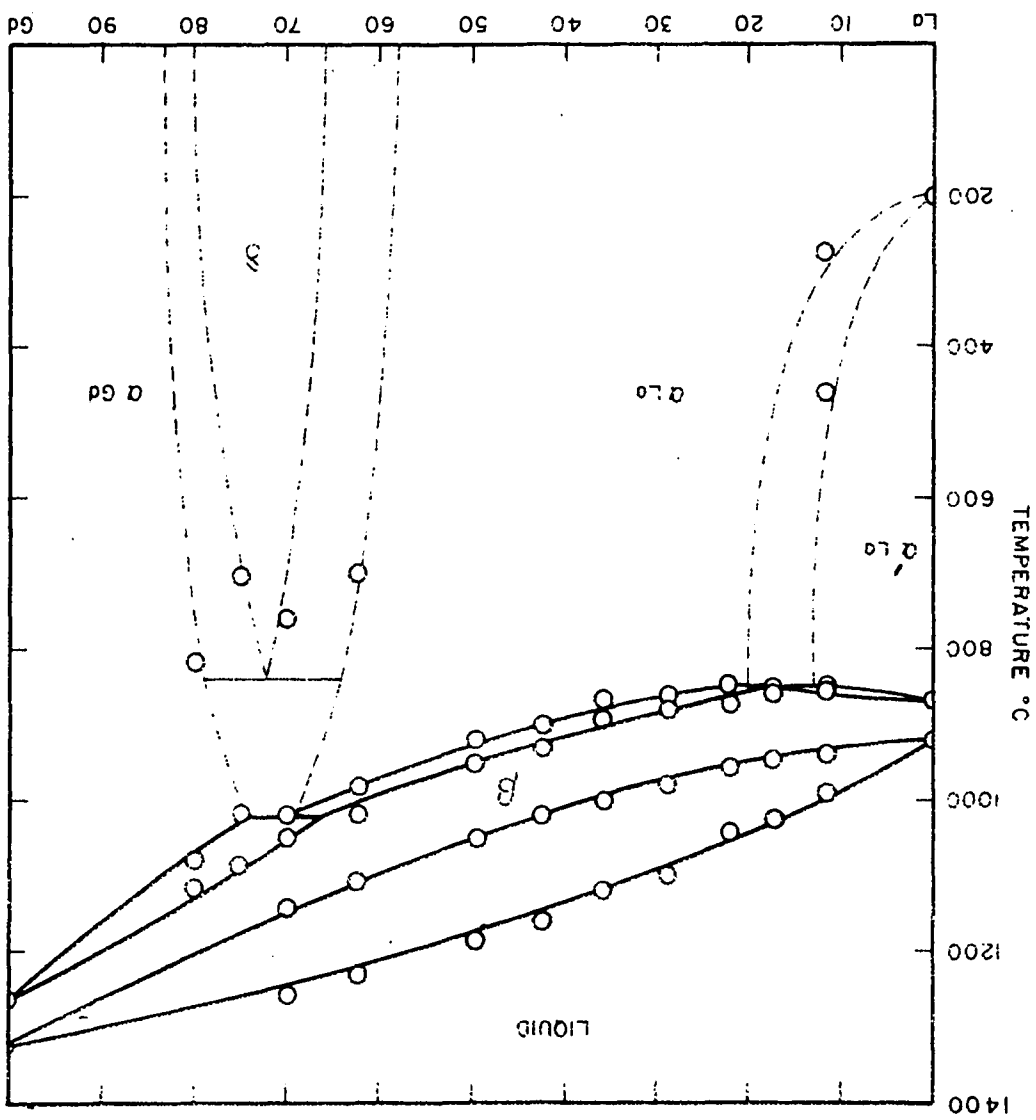
An excellent review of the literature dealing with the alloying behavior of the rare earths has recently been published by Gschneidner (1961). This author has critically examined the data on rare earth alloy systems that had been published up to April, 1960. With such a detailed summary available, the present survey will be concerned only with intra-rare earth alloys and their magnetic properties. It should perhaps be mentioned, however, that alloys of the rare earths with other transition metals exhibit very interesting magnetic properties. As representative of this field, one may cite the work of Nassau *et al.* (1960), in which the authors have determined the magnetic properties of intermetallic compounds formed between the rare earths and transition metals of the first long period, the ferromagnetism of  $YMn_4$ , observed by Myklebust and Daane (1962), the work of Bozorth *et al.* (1959), dealing with the magnetization of compounds of the rare earths with the platinum metals, and a study of the magnetic susceptibilities of cerium-thorium alloys, carried out by Bates and Newmann (1958).

Very little work has been carried out to date on the investigation of intra-rare earth binary alloy systems. Vogel and Klose (1954) have examined the lanthanum-cerium system,

and these authors find that complete solid solubility occurs between these two elements. Recently, Savitskii and Terekhova (1958) investigated the same system, and in addition carried out electrical resistivity measurements on a series of La-Ce alloys. The results of these investigations are in good agreement with each other, although the metals used in both studies were not of the highest purity. A preliminary survey of the lanthanum-neodymium system by Daane and Spedding (1954) has been modified slightly by Gschneidner (1961); complete solid solubility is observed in this system.

As previously noted, Valletta *et al.* (1962) studied the systems lanthanum-gadolinium, lanthanum-yttrium and gadolinium-yttrium. The same author has prepared  $\delta$ -phase alloys of cerium-yttrium, praseodymium-yttrium, neodymium-yttrium and neodymium-thulium. The La-Gd system is shown in Figure 1; the La-Y system is analagous, except that the composition of the  $\delta$  phase has been shifted from approximately 25 weight percent La, in La-Gd, to approximately 60 weight percent in La-Y. The gadolinium-yttrium system, as might be expected with two metals of the same crystal structure and approximately the same atomic radius, exhibits complete solid solubility. The only other intra-rare earth system that has been worked out in detail is the Ce-Y system (Lundin (1959)); this system is similar to those of La-Gd and La-Y, but the composition of the  $\delta$  phase differs from that reported by

Figure 1. The lanthanum-gadolinium equilibrium diagram



Valletta, in that the former reports it at 45 atomic percent yttrium, while the latter places it at 55 atomic percent yttrium. It may be also noted here that the present author found the  $\delta$  phase in Nd-Y to be of the composition 70 atomic percent Nd, while Valletta reports it as 53 atomic percent. This discrepancy will be discussed in the section of this work dealing with the preparation of alloys. Valletta's data on the composition and lattice parameters of the  $\delta$  phases are listed in the following table.

Table 2. Composition and lattice parameters of intra-rare earth  $\delta$  phases (Valletta, 1962)

Composition (atomic percent)	$a_0$ , Å	$c_0$ , Å
44.5 Ce - 55.5 Y	3.653	26.55
49.7 Pr - 50.3 Y	3.648	26.41
53.0 Nd - 47.0 Y	3.665	26.45
48.0 La - 52.0 Y	3.699	26.70
30.1 La - 69.9 Gd	3.667	26.48
63.0 Nd - 37.0 Tm	3.656	26.36

Magnetic properties have been determined for alloys of lanthanum-cerium (Roberts and Lock (1957)), lanthanum-neodymium (Lock (1957c)), gadolinium-lanthanum (Matthias et al. (1958); Thoburn et al. (1958b)), gadolinium-yttrium

(Thoburn et al. (1958b)), and europium-ytterbium (Beaver (1962)). Arajs and Miller (1960b) have used the data of Thoburn et al. to determine the spontaneous magnetizations for Gd-La and Gd-Y alloys. The data and conclusions of the papers dealing with magnetic properties of intra-rare earth alloys will be examined in detail in a later section; however, it is convenient to present the transition temperatures of these alloys in tabular form at this point. Table 3 lists, in  $^{\circ}\text{K.}$ , the Néel points ( $T_N$ ) and the Curie points ( $T_C$ ) that have been observed in these alloys. Curie points are listed as either paramagnetic,  $\theta_p$ , or ferromagnetic,  $\theta_f$ . The former is actually the parameter which occurs in the equation  $\chi = C/(T-\theta)$ , and is obtained by extrapolation of the curve of  $1/\chi$  vs.  $T$  to the point at which the curve intersects the temperature axis; the latter is the temperature at which the substance loses its spontaneous magnetization. The transition temperatures for the La-Nd alloys have been enclosed in parentheses, since it is not certain that these alloys are truly antiferromagnetic below these temperatures.

Table 3. Magnetic transition temperatures of intra-rare earth alloys

Alloy composition (atomic percent)	$T_N$	$T_C$	
		$\theta_p$	$\theta_f$
21.3 La - 78.7 Ce	9.5	-----	-----
63.7 La - 37.3 Ce	3.6	-----	-----
73.2 La - 26.8 Ce	1.9	-----	-----
95.1 La - 4.9 Ce	-----	-----	-----
27.4 La - 72.6 Nd	(9.1)	-----	-----
57.4 La - 42.6 Nd	(10.4)	-----	-----
80.1 La - 19.9 Nd	(4.8)	-----	-----
97.0 La - 3.0 Gd	-----	-----	1.4
96.5 La - 3.5 Gd	-----	-----	1.8
96.0 La - 4.0 Gd	-----	-----	2.0
94.0 La - 6.0 Gd	-----	-----	3.0
92.0 La - 8.0 Gd	-----	-----	4.0
90.0 La - 10.0 Gd	-----	-----	6.0
53.4 La - 46.6 Gd	<20	-----	-----
25.0 La - 75.0 Gd	130	70	-----
16.7 La - 83.3 Gd	155	172	-----
10.0 La - 90.0 Gd	-----	260	258
25 Gd - 75 Y	111	102	-----
50 Gd - 50 Y	182	186	-----
60 Gd - 40 Y	197	217	95
66.7 Gd - 33.3 Y	-----	229	211
75 Gd - 25 Y	-----	252	241
83.3 Gd - 16.7 Y	-----	266	262
90 Gd - 10 Y	-----	280	281
1 Eu - 99 Yb	-----	-----	-----
10 Eu - 90 Yb	-----	27.0	26.7
20 Eu - 80 Yb	-----	30.7	22.4
30 Eu - 70 Yb	5	27.7	-----
40 Eu - 60 Yb	8	14.0	-----

## III. EXPERIMENTAL PROCEDURE

The paramagnetic susceptibilities of the alloys were determined using two different techniques. The Gouy method, which involves the determination of the force on a sample due to a high magnetic field, was employed from 77 - 300°K. From 4.2 - ca. 100°K., the susceptibilities were determined by measuring the change in mutual inductance produced by moving the sample inside a coil system, using an a.c. bridge to measure the inductance. If the Gouy technique were employed down to 4.2°K., it would be necessary to operate the electromagnet with a gap between the pole pieces of about three inches, since a double Dewar system is required to reach these temperatures. At this gap distance, horizontal gradients in the field, arising from slight inhomogeneities, would make accurate force measurements very difficult, since such gradients would cause the sample to pull to the side and rub against the tube in which it is suspended. Therefore the inductance technique, which requires no external field, was employed for the low temperature measurements. Both techniques will be explained in the following discussions of experimental procedure.



## A. The Gouy Method for the Measurement of Paramagnetic Susceptibilities

### 1. Theory

The force on a magnetic dipole,  $m$ , has an x-component given by

$$F_x = m_x \left( \frac{\partial H_x}{\partial x} \right) + m_y \left( \frac{\partial H_y}{\partial x} \right) + m_z \left( \frac{\partial H_z}{\partial x} \right) .$$

If, instead of a permanent dipole, one has a particle of magnetizable matter of susceptibility  $k$  and volume  $v$ , its moment will be

$$\underline{m} = k \mu_0 v \underline{H} ,$$

and the x-component of the force on it is

$$\begin{aligned} F_x &= k \mu_0 v \left[ H_x \left( \frac{\partial H_x}{\partial x} \right) + H_y \left( \frac{\partial H_y}{\partial x} \right) + H_z \left( \frac{\partial H_z}{\partial x} \right) \right] \\ &= \frac{1}{2} k \mu_0 v \left( \frac{\partial H^2}{\partial x} \right) . \end{aligned}$$

If the particle has a susceptibility  $k_1$ , and is immersed in a medium with susceptibility  $k_2$ , then the force on it is

$$F_x = \frac{1}{2} (k_1 - k_2) \mu_0 v \left( \frac{\partial H^2}{\partial x} \right) .$$

This can be seen from the fact that any displacement of the

particle in the x-direction requires an opposite displacement of an equal volume of the surrounding medium.

Now if a cylindrical sample of matter is suspended between the poles of a magnet so that one end of the sample is in a region of large field strength and the other in a region of negligible field, then the force acting on the sample is that described by the latter equation, integrated over all layers from the region of maximum field out to the region of negligible field. If the cross section of the specimen is A, the vertical force in the x-direction is  $dF_x$  on an element  $A dx$ , and hence the total force is found, by integrating over the length of the specimen, to be

$$\begin{aligned} F_x &= \frac{1}{2} A \mu_0 (k_1 - k_2) \int \left( \frac{\partial H^2}{\partial x} \right) dx \\ &= \frac{1}{2} A \mu_0 (k_1 - k_2) (H_1^2 - H_2^2) \end{aligned}$$

where  $H_1$  is the field at the lower end of the specimen and  $H_2$  that at the upper end; usually,  $H_2^2$  is negligible compared with  $H_1^2$ .

The permeability,  $\mu_0$ , may be taken as unity, and  $k_2$  can be neglected in comparison to  $k_1$ , so we are left with the following expression for the force:

$$F_x = (1/2) A k_1 H_1^2 .$$

Thus, although the force arises from the inhomogeneous field at the edge of the pole tips, only the value of the homogeneous field at the center of the pole face is required. With field strengths of the order of  $10^3 - 10^4$  oersteds, forces ranging from milligrams to one or two grams are obtained, which can be measured on an ordinary analytical balance.

To make a measurement, the specimen is weighed when the electromagnet is excited, and again when it is not; the difference in weight,  $\Delta w$ , represents the magnetic pull on the specimen. Hence

$$(k/2) A H^2 = \Delta w g \text{ dynes } ,$$

where  $g$  is the gravitational constant. Now the susceptibility,  $k$ , is the susceptibility per unit volume; the susceptibility per unit mass is the quantity usually referred to in theoretical discussions, and is denoted by  $\chi$ . Since  $\chi = k/d$ , where  $d$  is the bulk density of the substance, we have from the above equation

$$\chi = 2 g (\Delta w/H^2)/Ad .$$

Now note that  $Ad = \text{cm}^2 (\text{g/cm}^3) = \text{g/cm} = \text{mass per unit height}$ . This quantity we shall denote by  $\rho$ . Substitution into the above equation leads to the final expression:

$$\chi = (2g/\rho) (\Delta w/H^2) .$$

More detailed descriptions of this method can be found in books on experimental magnetism (Selwood (1956); Bates (1951)). The Gouy method gives an absolute measurement of the susceptibility, with the accuracy of the method depending on  $\chi$  being constant with  $H$ , and  $\rho$  being constant with height. The former requirement is met very well by the rare earths, whose susceptibilities are quite well behaved in the paramagnetic region. The latter condition may produce errors as large as 2% if a powdered specimen is used, but this error is reduced considerably when a solid rod of material is used.

## 2. Apparatus

A four-inch, single-yoked, water-cooled electromagnet, constructed in this laboratory, was used in the present investigations. The pole pieces were designed with a two-inch diameter flat section at the center, which afforded a region of uniform field near the bottom of the sample. From the edge of the flat section to the outside, the pole pieces were tapered to avoid large gradients; if the gradients were very large, a small length of the sample would contribute most of the force, thereby increasing the possibility of error.

The 20 amperes and 200 volts required by the magnet at maximum field were supplied by a direct current generator, and the current through the magnet coils was regulated by a

current controller, designed and constructed in this laboratory, which reduced current fluctuations to about  $2 \times 10^{-4}$  ampere. It was found that magnetic fields could be reproduced to one part in one thousand by increasing the current to a maximum and then reducing it to a predetermined value. The fields were measured with a Pound magnetometer, manufactured by the Laboratory for Electronics, Inc. This instrument makes possible extremely accurate determinations of field strength, utilizing the principle of nuclear magnetic resonance. The magnet, current controller and magnetometer were first assembled for use in a study of the paramagnetic susceptibilities of chromium halides carried out by Hansen (1956).

A schematic drawing of the Gouy apparatus is given in Figures 2 and 3. The balance used was a Mettler one-pan, air-damped analytical balance, especially designed for the suspension of samples below the pan. Weights can be added or subtracted very rapidly by means of controls protruding from the front of the balance case, and the accuracy of a weighing is  $\pm 0.2$  mg. The balance was made reasonably airtight through the use of pressure sensitive tape, impregnated with fiberglass, which was used to seal all of the openings through which air might enter the balance case. The space between the bottom of the balance and the metal plate on which it rested was also sealed with this tape. The sample was

Figure 2. Schematic drawing of the Gouy apparatus--  
balance and support

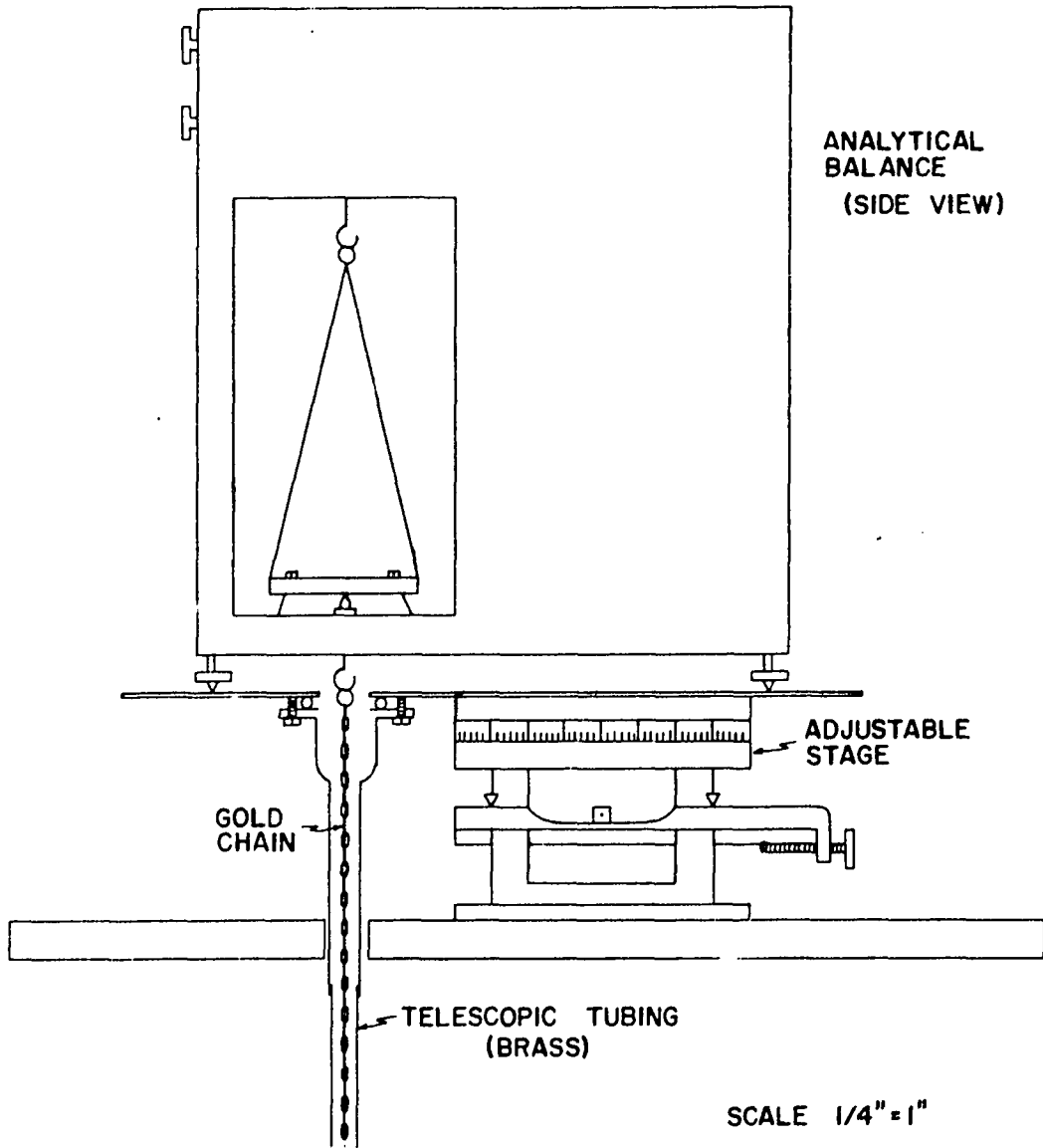
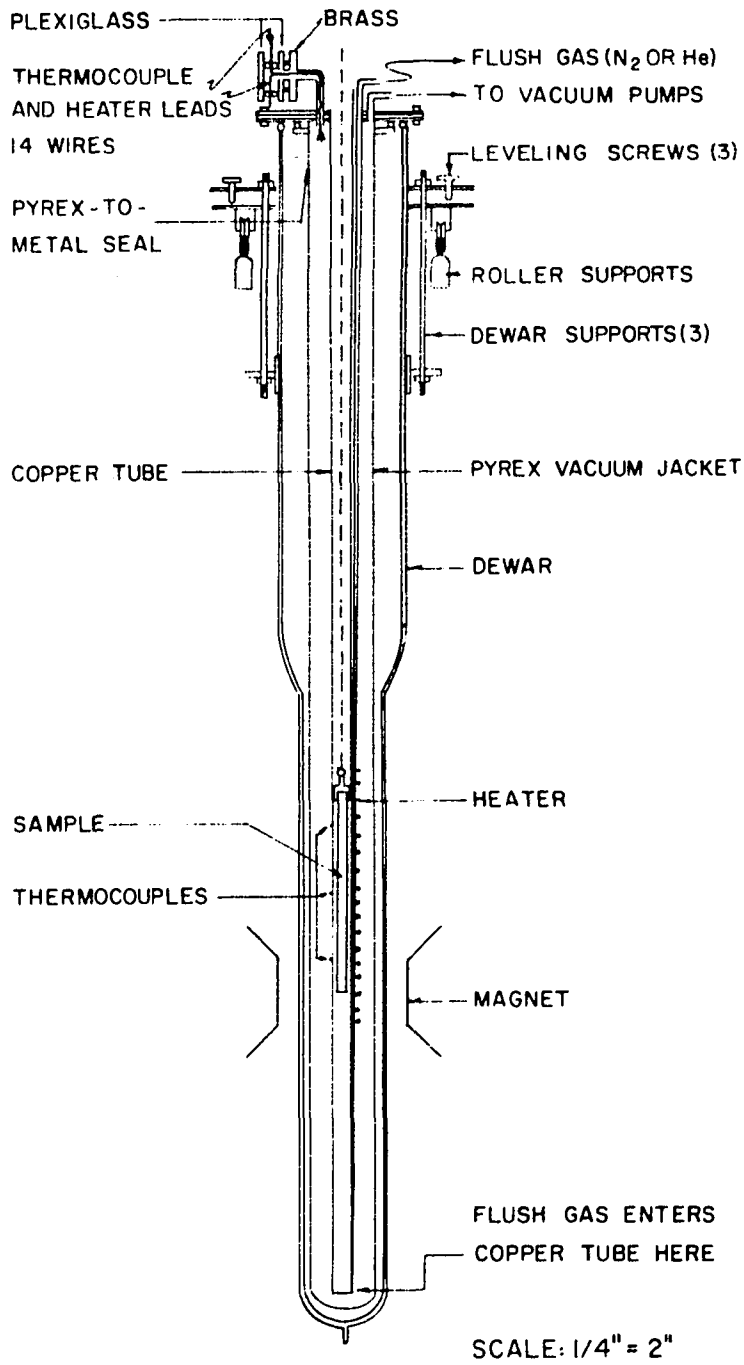


Figure 3. Schematic drawing of the Gouy apparatus--  
dewar assembly





suspended from the balance by means of a non-corrosive, non-magnetic gold chain, which hung in a gas-tight copper tube, in an atmosphere of helium or nitrogen, both of which are diamagnetic. Nitrogen gas was used most frequently, because its molecular weight is close to that of air; thus the damping mechanism of the balance was not affected as much as when helium gas was used. The gas was allowed to flow slowly past the sample and up into the balance case, to prevent air, which contains paramagnetic oxygen, from diffusing down the tube in which the sample was suspended. The gas was passed through a flowmeter, to ensure a constant flow rate.

Three copper-constantan thermocouples were soldered to the outside of the copper tube; they were so placed that, if one were to imagine the sample divided into three equal lengths, one thermocouple would be at the center of each portion. Each thermocouple was made up of three #30 B and S gauge constantan wires and one #36 gauge copper wire. It has been found that spurious emfs, due to inhomogeneities in the composition of the wire, are of the order of three microvolts in the constantan wire; the use of three such wires will decrease the spurious emfs to about one microvolt. The three thermocouples were calibrated by soldering them to a copper block together with a standard copper-constantan thermocouple which had been calibrated against a platinum resistance thermometer. The block was placed in a double dewar system

which allowed the temperature to be varied from 4.2°K. to 300°K. By means of this procedure, one was able to measure temperatures to within  $\pm 0.5^\circ$ .

In order to be able to control temperature variation between 77°K. and 300°K., the following procedure was used: a vacuum jacket made of Pyrex tubing was constructed to fit snugly around the copper tube in which the sample was suspended. This jacket, through a glass to metal seal, was soldered to a brass ring, which in turn was connected via an "O"-ring seal to the brass head of the apparatus. By pumping a high vacuum between the copper tube and the Pyrex jacket, the sample could be thermally isolated from the liquid nitrogen contained in the dewar. An electric heater, consisting of copper-beryllium wire, was wound non-inductively around that portion of the copper tube which contained the sample; an alternating current, of the order of 100 milliamperes, was supplied to the heater through the use of two ganged variacs. The usual procedure involved the following steps: a room temperature measurement was made, and then the dewar was filled with liquid nitrogen; a measurement of the susceptibility was then made at 77°K., and the space between the Pyrex jacket and the copper tube was pumped out to a pressure of about  $1 \times 10^{-5}$  millimeters of mercury. The heater was then turned on, and the sample allowed to warm slowly. A complete run from 77 - 300°K. was usually carried out in

about eight hours.

Because slight inhomogeneities in the magnetic field produce horizontal gradients that tend to pull the sample sideways and cause it to rub against the inner wall of the copper tube, the alloys of very high moment, La-Gd and Nd-Tm, were placed in a Gouy tube for the susceptibility measurements. The Gouy tube used was made of precision bore Pyrex tubing, about sixteen inches in length. The tube is divided into two sections by a glass septum fused inside the tube; when in use, the glass septum was placed at the center of the pole face. Since the tube extended in both directions from the center of the field, there was little net force on it. The alloy rod, approximately 15 cm. long and 0.5 cm. in diameter, was placed in the upper half of the tube, and the lower portion contained three lead weights, sealed in helium. The heavy weights served to keep the tube from swaying in the field, and allowed accurate weighings to be made. The alloys of lower moment, Nd-Y and Ce-Y, were only slightly affected by the horizontal gradients, and the use of a Gouy tube was not required.

In order to measure the force on the sample due to the field, a weighing was first made while the sample was in the field, and the temperatures indicated by the three thermocouples were recorded. The magnet, being mounted on rollers, could then be rolled away from the dewar, and another weighing made while the sample was out of the field.

## B. Susceptibility Measurements by the Mutual Inductance Bridge Method

### 1. Theory

The Hartshorn mutual inductance bridge used in this work was designed and constructed by Jennings (1960), and a detailed account of the use of such a bridge in magnetic susceptibility measurements is given by Gerstein (1960). Basically, the "primary" half of the circuit consists of an oscillator in series with a power amplifier, which in turn is connected in series with the bridge primary, an external variable primary, and the sample primary. The secondary half of the circuit consists of the bridge secondary in series with an external variable secondary, the sample secondary, and a 1:200 gain transformer. The output of the transformer was fed into a 33 cycle high gain amplifier, and from there to the Y terminals of an oscilloscope. The entire circuit is used essentially as a null point instrument, in that the bridge was used to oppose the signal from the sample coils due to the presence of the sample.

Now if we have a spherical sample of radius  $r$ , and if the primary and secondary are coaxial with length  $L$ , then, as long as  $(L/2) > 4r$ , we can write (ignoring demagnetization effects for the time being):

$$\Delta M = \left(\frac{n_S}{L_S}\right) \left(\frac{n_P}{L_P}\right) \mu_0 k V ,$$

where  $\Delta M$  is the change in mutual inductance of the coils, in henries, due to the presence of the sample,  $(n_S/L_S)$  and  $(n_P/L_P)$  are the numbers of turns per unit lengths for the secondary and primary coils, respectively,  $\mu_0$  is the permeability,  $k$  is the volume susceptibility and  $V$  is the volume of the sample. Dividing both sides of this equation by  $N$ , where  $N$  is the number of moles of sample, and denoting the constant terms by  $\beta$ , we have:

$$(\Delta M/N) = \beta \chi_g d (V/N) ,$$

since  $\chi_g$ , the susceptibility per unit mass, is equal to  $k/d$ , where  $d$  is the density. Now note that  $(V/N)$  is the molar volume, and

$$\chi_g d V_m = \chi_m ,$$

i.e., the molar susceptibility, since

$$\chi_m = (\text{molecular weight}) \chi_g = V_m d \chi_g .$$

Therefore, we find that

$$(\Delta M/N) = \beta \chi_m .$$

In this expression, as in those above,  $\Delta M$  is given in henries;

however, it is convenient to be able to measure this quantity in terms of the number of turns of wire involved. In order to be able to do this, the apparatus is calibrated with a standard paramagnetic salt (in this case, manganous ammonium sulphate was used). We have then

$$(\Delta M/N) = \gamma \chi_m ,$$

where now  $\Delta M$  is in turns, and  $\gamma$  is called the coil constant, and is determined by the calibration procedure. For this work,  $\gamma = 4595$ .

If demagnetization effects are not ignored, the starting equation becomes, for a spherical sample,

$$\frac{\Delta M}{N} = \frac{n_S n_P}{L_S L_P} \frac{\mu_0 \chi_m}{\left(1 + \frac{\chi_m}{3V_m}\right)} .$$

An examination of the data shows that a correction of the order of 1% is introduced by taking into account demagnetization effects. Since such a correction is within experimental error, these effects have been ignored in the present work.

## 2. Experimental

A sample holder was made from a length of 5/8 inch bakelite rod, by merely cutting a three inch length in half, and machining out hemispherical cavities in one end of each

half. When the two halves were rejoined, the spherical sample fitted snugly between the two machined ends. A gold-2.1 atomic percent cobalt versus copper thermocouple was threaded through a small hole in the top half of the sample holder, and placed in contact with the sphere. The sample holder was then placed inside a heater, which consisted of copper-beryllium wire wound non-inductively on a cylinder of stiff paper. The heater coil containing the sample holder fit snugly at the bottom of a quartz tube, approximately 3-1/2 feet in length, and the leads for the heater and thermocouple were wound, for a length of about three feet, around a piece of red fiber tubing (an insulating material), in order to decrease heat conduction along the wires.

The sample tube was placed inside a second quartz tube, on which the sample coils were wound. The connection between the two tubes was made through an "O"-ring slip seal, which permitted the sample tube to be raised and lowered, thus moving the sample in and out of the coils. The tube on which the coils were wound was immersed in the refrigerant contained in the inner dewar, the walls of this tube forming the inner wall of the inside dewar. The heater and thermocouple leads were led out of the sample tube through a length of rubber tubing; after greasing the wires and securing a hose clamp to the tubing, a vacuum could be pumped on the sample tube, removing air, which is paramagnetic, from the



system.

Temperatures were measured to within  $\pm 0.5^\circ$  by measuring the emf developed by the gold-cobalt thermocouple at  $4.2^\circ\text{K}$ ., and comparing this emf with the value obtained by Powell et al. (1961), who determined the emf vs. temperature curve for this thermocouple, using wire obtained from the same manufacturer (Sigmund Cohn and Corp.). A proportionality constant is thus obtained from this single calibration point, and this constant can be employed over the range  $4.2 - 77^\circ\text{K}$ ., since the relationship between temperature and  $dE/dT$  is a linear one over this range.

With the inner dewar filled with liquid helium and the outer with liquid nitrogen, helium exchange gas was bled into the sample tube and into the space between the inner dewar and the sample tube, in order to allow the sample to attain thermal equilibrium at  $4.2^\circ\text{K}$ . A measurement of the mutual inductance was made, and then the sample was removed from the coils, by sliding the sample tube upwards through the "O"-ring seal. Another inductance measurement was carried out, and the difference between the two inductances related to the susceptibility as outlined above. The exchange gas was then pumped from the space between the inner dewar and the sample tube, and the sample heated by passing a small direct current (0 - 100 ma.) through the heater coil. Periodic readings were taken with the sample out of the coils,

and an average "out" reading obtained. "In" readings were taken at approximately one-degree intervals, from 4.2 - ca. 80°K.

### C. Preparation of Alloys

The samples for Gouy measurements should be approximately 15 cm. in length and about 0.5 cm. in diameter. Casting a rod of this size presents certain difficulties: first of all, voids in the sample often develop when the melt freezes, and since the accuracy of the Gouy method depends to a large extent on the density of the sample remaining constant along its length, such voids could not be tolerated. Secondly, in order to ensure the homogeneity of the alloy, it should be held in the molten state for an appreciable length of time, but the reactivity of the rare earth metals is such that contamination by the crucible material is likely when such a procedure is followed. For these reasons, it was decided to prepare the rods by arc-melting the constituent metals together, and swaging the alloy into the desired shape. In the arc-melting procedure, small chunks of the constituent metals in the desired proportions were melted into the form of a button in an atmosphere of argon. The resulting button was inverted and remelted several times for homogenizing purposes, and finally melted down into a mold about five

inches long by  $3/8$  inch wide. This resulted in a cigar-shaped sample, which was inverted and remelted several times.

The elliptically shaped sample thus produced was then cold swaged until a cylinder was obtained, at which point annealing was usually necessary before further reduction in cross-section could be effected. After annealing for about eight hours at  $550 - 600^{\circ}\text{C}.$ , swaging was continued until the desired sample size was attained. For the alloys of high moment, La-Gd and Nd-Tm, the final diameter of the rods used was about 0.25 cm.; for those of lower moment, a diameter of 0.5 cm. was required to obtain weight changes of the order of 0.1 g. in the Gouy apparatus at room temperature.

The neodymium-thulium alloy could not be prepared by arc-melting, because the vapor pressure of thulium metal is high enough that a serious loss of this metal would occur during the melting procedure. This alloy was prepared by placing the metals together in a crucible made from 15 mil tantalum tubing,  $1/2$  inch in diameter, and melting the alloy by r-f induction methods. The crucible was sealed under a partial pressure of helium gas, and the operation was carried out in a high-vacuum system. The alloy was held in the molten condition, ca.  $1400^{\circ}\text{C}.$ , for approximately one hour, and then allowed to cool slowly through the melting point, to prevent the formation of voids. After radiographic examination showed the casting to be free from holes, the tantalum con-

tainer was turned off on a lathe, and the swaging operation outlined above was carried out to obtain a sample of the desired size.

After the final swaging operation, the alloys were annealed for approximately 2-3 hours at 550°C., to remove the effects of cold-working. The short annealing time was employed in order to avoid producing appreciable grain growth in the samples. Swaging tends to break up the large crystals formed during melting, and together with the recrystallization during annealing, reduced the risk of preferred orientation effects showing up in the magnetic measurements. The ends of the rods were faced off, and final surfaces cleaned by taking a very fine cut on the lathe, followed by a polishing operation using the type of polishing cloth employed in preparing samples for metallographic examination. The alloys were then weighed, and their lengths measured with a cathetometer. Micrometer readings were taken of the rod diameters at increments along the rods, and it was found that the diameters were constant to within 1%.

For the susceptibility measurements between 4.2 and 77°K., spherical samples were prepared; at these temperatures, demagnetization effects can become important, and the correction factor for samples of other than spherical geometries is difficult to determine. For a sphere, the demagnetization factor has been shown to be  $4\pi/3$ . A spherical

section could be obtained on one end of the rod by using a lathe tool whose cutting edge was in the shape of a hemisphere; this produced practically a complete sphere, with only a thin connection remaining between the sphere and the rod. This connection was severed with a jeweler's saw, and the sphere then hand-finished with 300 grit abrasive paper. Samples obtained in this manner were not truly spherical, but slightly ellipsoidal. The ratios of major to minor axes, as measured with a micrometer, varied from 1.02 (Nd-Tm) to 1.10 (La-Gd). The spheres, of course, could not be made any larger than the rod diameter; thus the La-Gd and the Nd-Tm samples were approximately 0.25 cm. in diameter, while the spheres of Nd-Y and Ce-Y were approximately 0.5 cm. in diameter.

Spectrographic analyses of the alloys used in these experiments are given in Table 4. The alloys were analyzed after preparation, to determine whether or not any impurities were introduced during the preparative procedure.

Table 4. Spectrographic analyses of the alloys investigated  
(concentrations given in parts per million)

Element	La-Gd	Nd-Tm	Nd-Y	Ce-Y
Ca	< 50	<200	< 50	< 50
Ce	-----	-----	-----	X
Co	-----	-----	-----	-----
Cr	<200	<200	<200	-----
Cu	<100	<500	<100	<100
Dy	-----	<100	-----	-----
Er	-----	<500	-----	-----
Eu	-----	-----	-----	-----
Fe	<500	<500	<500	<200
Gd	X	-----	-----	-----
Ho	-----	-----	-----	-----
La	X	-----	-----	-----
Lu	-----	-----	-----	-----
Mn	<200	<200	<200	-----
Nd	-----	-----	-----	<200
Ni	-----	-----	-----	-----
Pr	-----	-----	-----	-----
Sc	-----	-----	-----	-----
Si	<200	<200	<200	< 50
Sm	-----	-----	-----	-----
Ta	-----	<800	-----	<800
Tb	-----	-----	-----	-----
Ti	-----	-----	-----	-----
Tm	-----	X	-----	-----
Y	-----	-----	X	X
Yb	-----	-----	-----	-----

## IV. RESULTS

## A. X-ray Diffraction Data

Samples for x-ray analysis were obtained from both ends and the center of each rod, in order to confirm the homogeneity of the alloys. For annealing purposes, the filings were sealed, under helium, in a small container made from 1/8" tantalum tubing, which had previously been outgassed by heating in vacuo at an elevated temperature (ca. 1500°C.). The container was then placed inside a quartz tube, and the tube sealed off while a vacuum was being pumped on it. The tube was then placed in an annealing furnace, usually at about 500°C. for eight hours. After annealing, the filings were placed in Pyrex capillaries, and the x-ray diffraction patterns obtained with a Debye-Scherrer powder camera, using nickel-filtered copper radiation.

Tables 5 and 6 show the results obtained for the four alloys. While the La-Gd and the Nd-Tm alloys exhibited the samarium structure at the same compositions as reported by Valletta et al. (1962), it was found that the Nd-Y and Ce-Y alloys did not. Table 7 compares the compositions and lattice parameters obtained in this study with those of Valletta. One possible reason for the discrepancies observed in the Nd-Y and Ce-Y systems might have arisen from the method of

alloy preparation used in the two cases. Valletta, in order to obtain homogeneous alloys, allowed the molten alloy to equilibrate for an hour in a tantalum crucible, while the present author employed an arc-melting technique. Since yttrium picks up tantalum more readily than the other rare earths (except scandium), it is possible that tantalum contamination of the alloy stabilized the  $\delta$  phase at a different composition. In this connection, it should be noted that the Nd-Tm alloys were prepared in the same manner in both investigations, and the composition was reproducible.

#### B. Gouy Data

The data obtained, from 77 to 300°K., for the temperature dependence of susceptibility for the four alloys are listed in Tables 8, 10, 12, and 14. Theoretical values of the susceptibility were calculated at 50, 100, 150, 200, 250, and 300°K. for comparative purposes. A typical calculation is shown before for the Nd-Tm alloy:

Using the simplified Hund-Van Vleck equation, the susceptibility per gram is given by

$$\chi_g = (N/M) (g^2 \beta^2 J(J+1)) / 3kT .$$

Assuming that the alloy constituents are present as the tri-



positive ions, one has, for  $\text{Nd}^{+3}$ :

$$L = 6, \quad S = 3/2, \quad J = L - S = 9/2 .$$

Thus,

$$\begin{aligned} g &= 1 + (S(S+1) + J(J+1) - L(L+1)) / 2J(J+1) \\ &= 8/11 , \end{aligned}$$

and

$$\begin{aligned} \chi_g &= \frac{(6.025 \times 10^{23})(8/11)^2(0.9271 \times 10^{-20})^2(9/2)(9/2 + 1)}{(144.3)(3)(1.380 \times 10^{-16})T} \\ &= 11,330 \times 10^{-6}/T . \end{aligned}$$

For a 59.20 weight percent Nd alloy, one has

$$\chi_g = (0.5920) 11,380 \times 10^{-6}/T = 6,707 \times 10^{-6}/T .$$

Similarly, for the  $\text{Tm}^{+3}$  ion, one obtains

$$L = 5, \quad S = 1, \quad J = L + S = 6, \quad g = 7/6 .$$

For a 40.80 weight percent alloy,

$$\chi_g = 16,870 \times 10^{-6}/T .$$

Thus, at 300°K., the theoretical value for the gram susceptibility of the Nd-Tm alloy is

$$\begin{aligned}\chi_g(\text{alloy}) &= \frac{6,707 \times 10^{-6}}{300} + \frac{16,780 \times 10^{-6}}{300} \\ &= 77.70 \times 10^{-6} .\end{aligned}$$

The observed values for the gram susceptibility are denoted by the symbol  $\chi_g^*$ . This notation is used to indicate that the values have been corrected for the underlying diamagnetism due to the electrons in closed shells. The diamagnetic contribution of the La, Ce, Gd, and Tm cores has been taken to be  $-38 \times 10^{-6}$  emu., which is the value for the Xenon configuration, while that of yttrium is  $-20 \times 10^{-6}$  emu., as given by Klemm (1941).

For the alloys La-Gd, Nd-Y, and Ce-Y, in which the susceptibility of the alloy is essentially that of the paramagnetic metal, the values of  $\mu_{\text{eff}}$  for the paramagnetic atoms have been calculated from the observed susceptibility data as follows:

$$\mu_{\text{eff}}^2 = \frac{3 k \chi_m (T-\theta)}{N \beta^2} = 7.994 \chi_m (T-\theta)$$

In this expression,  $\theta$  is the paramagnetic Curie point, determined by extrapolation of the straight line portion of the  $1/\chi$  vs.  $T$  curve to the point at which the curve intersects the temperature axis. The four alloys exhibited the following values of  $\theta$ :

$$\text{La-Gd} = + 10^\circ$$

$$\text{Nd-Tm} = - 8^\circ$$

$$\text{Nd-Y} = - 24^\circ$$

$$\text{Ce-Y} = - 57^\circ$$

The values of  $\chi_m$  used in the equation above were obtained by dividing the observed  $\chi_g$  by the weight percent of the paramagnetic element in the alloy, and multiplying the resulting figure by the molecular weight of the element; e.g., for the La-Gd alloy, which contained 72.46 weight percent gadolinium,

$$\mu_{\text{eff}}^2 (\text{Gd}) = (7.994) (T-10) (157.3) \frac{\chi_g(\text{alloy})}{0.7246} .$$

The above procedure for calculating the effective moments cannot be applied to the Nd-Tm alloy, since in this case we are dealing with an alloy consisting of two paramagnetic atoms. Although the susceptibilities are additive, the moments are not, since the effective moments and the susceptibilities are not linearly related. One can, however, obtain a measure of the effective moments as follows: rewriting the fundamental equation for the gram susceptibility we have

$$\chi_g = (N/M) \beta^2 g^2 J(J+1)/3kT = (N\beta^2/3kMT) \mu_{\text{eff}}^2 .$$

Now, assuming a Curie-Weiss relationship we can express the gram susceptibility of an alloy consisting of elements A and B in the following manner:

$$\chi_g = (N\beta^2/3k) \frac{(\text{wt.}\% \text{ A})(\mu_A^2)}{M_A(T-\theta_A)} + \frac{(\text{wt.}\% \text{ B})(\mu_B^2)}{M_B(T-\theta_B)} .$$

If one makes the assumption that  $\theta_A$  and  $\theta_B$  are those of the pure metals, the effective moments can be determined from a knowledge of  $\chi_g$  at two temperatures. In principle, one could set up this equation at four temperatures, and thus determine all four unknowns; however, this procedure rapidly becomes unwieldy, and the equations extremely difficult of solution. The value employed for  $\theta_{Nd}$  was  $+4^\circ$ , as determined by Lock (1957a), and for Tm,  $\theta = +20^\circ$ , from Rhodes *et al.* (1958). The two temperatures employed were  $301.1^\circ\text{K.}$ , where  $\chi_g(\text{alloy}) = 70.19 \times 10^{-6}$  emu, and  $78.4^\circ\text{K.}$ , where  $\chi_g(\text{alloy}) = 264.4 \times 10^{-6}$  emu. Simultaneous solution of the two equations yielded the following values of  $\mu_{\text{eff}}$ :

$$Nd = 3.42 \text{ Bohr magnetons}$$

$$Tm = 6.82 \text{ Bohr magnetons}$$

The theoretical values, given by the relation  $\mu_{\text{eff}}^2 = g^2 J(J+1)$ , are 3.68 and 7.56 Bohr magnetons, respectively.

Field dependence measurements were carried out on all four alloys, in order to ensure that no ferromagnetic impurity was present. These measurements were carried out at  $300^\circ\text{K.}$ , and are listed in Table 16. The effect of varying the field

on the susceptibility of the alloys is seen to be negligible.

The susceptibility data obtained from 77 - 300°K. have been plotted as  $1/\chi_g$  versus T in Figures 5, 7, 9, and 11. In addition, Figure 4 shows the temperature dependence of Mohr's salt ( $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ), which is usually employed as a susceptibility standard, obeying the relation

$$\chi_g = 9500 \times 10^{-6} / (T + 1) .$$

Although the Gouy method is an absolute method for the determination of susceptibilities, and hence requires no calibration procedure, this standard was run in order to be sure that the complete apparatus was functioning properly. All of the points but one fall either on or just below the straight line given by the above equation, and the average deviation was found to be 1.9%. Since the usual experimental error involved in measuring the susceptibility of a powdered specimen by this method is 2%, one is assured that the apparatus was functioning correctly.

For the La-Gd alloy, the curve of  $1/\chi_g$  vs. T follows a Curie-Weiss law from 300 - 155°K. Over this range, the gram susceptibility increases from a value which is 37% higher than theory at 300°K., to one which is 51% higher at 155°K. There is a slope change at 155°K., and another at 128°K.; from 125 - 77°K., the susceptibility remains roughly constant. The Nd-Y alloy was found to be very well behaved

over the range 77 - 300°K., the slope of the  $1/\chi_g$  vs. T curve for this alloy differing only slightly from that expected from theory. The gram susceptibility varied from 12% lower than theory, at 77°K., to 1.5% higher, at 300°K.

The Nd-Tm and Ce-Y alloys were also well-behaved over the temperature range 77 - 300°K., although there do appear to be two slight changes in slope in the curve for the former alloy, at 250 and 200°K. The observed susceptibilities for Nd-Tm are lower than the theoretical values, ranging from 8.7% low at 300°K., to 7.4% low at 77°K. For the Ce-Y alloy, the observed susceptibilities are markedly lower than the theoretical values, ranging from 11.2% low at 300°K., to a value which is 35.8% lower at 77°K.

### C. Mutual Inductance Data

The susceptibility data obtained on the alloys by the mutual inductance technique are listed in Tables 9, 11, 13, and 15. The curves of  $1/\chi_g$  vs. T obtained from this data are plotted along with the Gouy data in the figures listed above, and separately in Figures 6, 8, 10, and 12. The observed susceptibilities are in good agreement with those measured by the Gouy method only in the case of the Nd-Y alloy. For the La-Gd alloy, the inductance technique gives a value which is about 28% higher than the value

obtained using the Gouy method, while in the Nd-Tm and Ce-Y alloys, the data obtained from the inductance measurements is 42 and 52% higher, respectively. These are maximum deviations, obtained over a temperature range of approximately ten degrees, in which the data from the two techniques overlap.

Well-defined minima were observed in the  $1/\chi_g$  vs.  $T$  curves for the Nd-Y and Nd-Tm alloys, at 34.5°K. and 28.5°K., respectively. As mentioned above, a region of constant susceptibility was found to exist for the La-Gd alloy, from 125 - 77°K.; mutual inductance data showed that the susceptibility remains roughly constant all the way down to approximately 7°K., where a small peak occurs in the curve. There exists a small region of constant susceptibility in the Ce-Y alloy also, from 26 - 37°K. These anomalies will be discussed in detail in the following section.

Table 5. Comparison of observed and calculated  $\sin^2\theta$  values for the La-Gd and Nd-Y  $\delta$ -phase alloys

La-Gd		h k l	Nd-Y	
Obs. $\sin^2\theta$	Calc. $\sin^2\theta$		Obs. $\sin^2\theta$	Calc. $\sin^2\theta$
0.0602	0.0597	101	0.0608	0.0605
		102	0.0640	0.0631
0.0683	0.0680	009	0.0705	0.0697
0.0735	0.0723	104	0.0746	0.0734
0.0795	0.0799	105	0.0814	0.0812
0.1031	0.1001	107	0.1028	0.1018
0.1114	0.1126	108	0.1151	0.1147
0.1428	0.1429	10,10	0.1458	0.1457
0.1628	0.1605	10,11	0.1629	0.1637
0.1766	0.1766	110	0.1790	0.1790
0.2016	0.2008	10,13	0.2047	0.2050
0.2247	0.2235	10,14	0.2274	0.2282
0.2454	0.2447	119	0.2485	0.2487
0.2565	0.2565	205	0.2588	0.2602
0.2742	0.2722	00,18	0.2785	0.2786
		10,19	0.3778	0.3771
		10,20	0.4051	0.4037
0.4283	0.4255	214	0.4335	0.4315
0.4509	0.4505	20,16		
		11,18	0.4552	0.4576
		218	0.4726	0.4727
		10,23	0.5136	0.5146
		305	0.5597	0.5585
		21,14	0.5848	0.5862
0.5988	0.5979	309	0.6044	0.6067
	0.6124	{00,27}		0.6269
0.6133	0.6138	{30,10}	0.6223	0.6230
0.6905	0.6944	30,14		
	0.7726	{30,17}		
0.7752	0.7745	{229}		
	0.7787	314		
		10,29	0.7822	0.7829
		21,19		0.7822
		315	0.7985	0.7972
0.7925	0.7890	11,27	0.8096	0.8060
0.8051	0.8033	20,26	0.8217	0.8200



Table 6. Comparison of observed and calculated  $\sin^2\theta$  values for the Nd-Tm and Ce-Y  $\delta$ -phase alloys

Nd-Tm		h k l	Ce-Y	
Obs. $\sin^2\theta$	Calc. $\sin^2\theta$		Obs. $\sin^2\theta$	Calc. $\sin^2\theta$
0.0619	0.0611	101		
0.0648	0.0637	102	0.0642	0.0630
0.0710	0.0705	009	0.0701	0.0697
0.0774	0.0744	104	0.0739	0.0733
0.0792	0.0811	105	0.0778	0.0810
0.1007	0.1028	107	0.0994	0.1007
0.1181	0.1159	108	0.1179	0.1146
0.1499	0.1472	10,10	0.1514	0.1455
0.1693	0.1655	10,11	0.1671	0.1636
0.1806	0.1806	110	0.1786	0.1786
0.2091	0.2072	10,13	0.2019	0.2049
0.2350	0.2307	10,14		
0.2508	0.2511	119	0.2470	0.2483
		204	0.2542	0.2514
0.2836	0.2819	00,18	0.2758	0.2786
0.2987	0.2965	208		
		20,13	0.3906	0.3885
0.3995	0.4012	10,20		0.4035
		20,14	0.4094	0.4067
0.4391	0.4354	214	0.4318	0.4305
		11,18		0.4573
		20,16	0.4535	0.4583
0.4625	0.4641	217		0.4589
0.4974	0.4922	20,17	0.4857	0.4867
		301	0.5328	0.5367
0.5782	0.5732	306	0.5667	0.5668
0.6074	0.6124	309	0.6002	0.6055
		00,27		0.6269
		30,10	0.6206	0.6219
0.6727	0.6729	21,17	0.6633	0.6653
		220	0.7109	0.7103

Table 7. Comparison between compositions and lattice parameters of the  $\delta$ -phase alloys obtained in the present study with those of Valletta (1961)

Composition, atomic percent		Lattice parameters, Å	
Valletta	This study	Valletta	This study
44.5 Ce - 55.5 Y	55.0 Ce - 45.0 Y	a = 3.653 c = 26.55	a = 3.648 c = 26.35
53.0 Nd - 47.0 Y	70.0 Nd - 30.0 Y	a = 3.665 c = 26.45	a = 3.644 c = 26.28
30.1 La - 69.9 Gd	30.1 La - 69.9 Gd	a = 3.667 c = 26.482	a = 3.667 c = 26.44
63.0 Nd - 37.0 Tm	63.0 Nd - 37.0 Tm	a = 3.656 c = 26.36	a = 3.628 c = 26.13

Table 8. Temperature dependence of the paramagnetic susceptibility of the La-Gd  $\delta$ -phase alloy (72.46 wt. % Gd); field strength = 1640 oersteds

T, °K	$\chi_g(\text{theo}) \times 10^6$	$\chi_g^* \times 10^6$	$\frac{1}{\chi_g^*} \times 10^{-3}$	$\mu_{\text{eff}}$ (Gd)
50.00	728.5			
78.29		531.8	1.880	7.92
78.82		534.2	1.872	
80.58		535.3	1.868	
82.98		534.6	1.871	
86.47		528.6	1.892	
88.21		527.2	1.897	
89.60		525.2	1.904	
92.35		522.4	1.914	
98.22		514.0	1.946	
99.14		515.0	1.942	8.92
100.0	364.3			
106.2		511.2	1.956	
109.0		508.0	1.969	
112.2		507.0	1.972	
114.7		504.5	1.982	
118.0		495.1	2.020	
122.5		474.1	2.109	
126.0		441.5	2.265	9.43
128.9		457.3	2.187	
132.0		421.6	2.370	
132.5		425.4	2.351	
136.5		422.6	2.366	
142.7		402.3	2.486	
150.1	243.0	384.5	2.601	9.66
152.5		372.9	2.682	
156.5		351.2	2.847	
162.6		335.4	2.982	
169.2		323.7	3.089	
173.4		313.7	3.188	9.42

Table 8 (Continued)

T, °K	$\chi_g(\text{theo}) \times 10^6$	$\chi_g^* \times 10^6$	$\frac{1}{\chi_g^*} \times 10^{-3}$	$\mu_{\text{eff}}$ (Gd)
183.5		291.7	3.428	
188.4		282.9	3.535	
192.5		274.2	3.647	
199.1		265.0	3.774	9.32
200.0	182.2			
209.4		254.6	3.928	
213.9		248.4	4.026	
220.0		241.6	4.139	
225.2		234.6	4.263	9.36
231.1		228.9	4.369	
237.9		220.8	4.529	
250.0	145.8			
251.6		210.2	4.757	9.39
264.0		200.3	4.993	
273.2		194.1	5.152	9.41
287.0		184.6	5.417	
300.0	121.5			
300.4		166.8	5.995	9.16

Table 9. Temperature dependence of the paramagnetic susceptibility of the La-Gd  $\delta$ -phase alloy (72.46 wt. % Gd); zero field measurements

T, °K	$\chi_g^* \times 10^6$	$\frac{1}{\chi_g^*} \times 10^{-3}$	T, °K	$\chi_g^* \times 10^6$	$\frac{1}{\chi_g^*} \times 10^{-3}$
4.2	772.2	1.295	49.51	786.6	1.271
5.92	784.0	1.276	51.63	777.4	1.286
6.94	778.1	1.285	53.88	722.8	1.294
8.01	805.6	1.241	55.92	766.9	1.304
9.33	858.2	1.165	57.92	762.3	1.312
10.42	89.10	1.122	59.90	759.7	1.316
11.53	901.5	1.109	62.17	758.4	1.319
12.27	912.7	1.096	64.25	758.4	1.319
14.02	925.1	1.081	66.93	759.0	1.318
16.09	925.8	1.080	70.03	767.6	1.303
18.21	931.7	1.073	71.87	763.0	1.311
20.23	921.2	1.086	75.00	762.3	1.312
22.46	908.7	1.100	77.14	753.8	1.327
24.19	895.6	1.117	78.92	753.1	1.328
26.72	877.9	1.139	80.84	748.5	1.336
28.90	868.7	1.151	83.34	759.7	1.316
30.82	853.6	1.172	85.23	757.1	1.321
32.77	844.4	1.184	86.96	760.3	1.315
34.81	833.9	1.199	89.25	771.5	1.296
37.20	828.0	1.208	90.95	776.1	1.288
39.50	820.1	1.219			
41.49	811.6	1.232			
43.43	801.7	1.247			
45.51	794.5	1.259			
47.53	793.2	1.261			

Table 10. Temperature dependence of the paramagnetic susceptibility of the Nd-Tm  $\delta$ -phase alloy (59.20 wt. % Nd); field strength = 2180 oersteds

T, °K	$\chi_g(\text{theo}) \times 10^6$	$\chi_g^* \times 10^6$	$\frac{1}{\chi_g^*} \times 10^{-3}$
50.00	466.1		
78.38		264.7	3.778
83.92		258.4	3.870
88.20		251.0	3.984
91.53		243.2	4.112
95.07		233.6	4.281
97.73		227.8	4.390
100.0	233.1		
101.5		219.4	4.558
105.7		210.8	4.744
110.4		200.8	4.980
115.7		119.4	5.225
124.3		176.1	5.679
128.2		168.4	5.938
131.9		162.1	6.169
136.4		155.6	6.427
140.2		151.1	6.618
144.9		146.9	6.807
150.0	155.4		
152.0		141.2	7.082
156.1		137.9	7.252
160.3		134.8	7.418
164.6		131.0	7.634
169.0		127.9	7.819
172.9		125.0	8.000
177.9		121.4	8.237
182.8		118.3	8.453
189.6		114.5	8.734
196.0		110.8	9.025
200.0	116.5		

Table 10 (Continued)

T, °K	$\chi_g(\text{theo}) \times 10^6$	$\chi_g^* \times 10^6$	$\frac{1}{\chi_g^*} \times 10^{-3}$
201.4		107.8	9.276
207.0		104.8	9.542
212.8		102.0	9.804
216.7		99.48	10.05
221.0		96.34	10.38
224.9		94.79	10.55
229.0		92.82	10.77
233.2		91.02	10.99
237.4		89.05	11.23
241.2		87.53	11.42
246.0		85.61	11.68
250.0	93.24		
250.7		83.88	11.92
254.0		82.66	12.10
259.0		80.99	12.35
264.7		79.02	12.66
270.2		77.56	12.89
276.1		75.76	13.20
281.5		74.61	13.40
287.0		73.27	13.65
293.4		72.24	13.84
300.0	77.70		
301.1		70.44	14.20

Table 11. Temperature dependence of the paramagnetic susceptibility of the Nd-Tm  $\delta$ -phase alloy (59.20 wt. % Nd); zero field measurements

T, °K	$\chi_g^* \times 10^6$	$\frac{1}{\chi_g^*} \times 10^{-3}$	T, °K	$\chi_g^* \times 10^6$	$\frac{1}{\chi_g^*} \times 10^{-3}$
4.2	1617	0.6184	39.59	1224	0.8170
4.77	1633	.6124	41.57	1125	.8889
5.68	1645	.6079	43.50	1040	.9615
5.77	1587	.6301	45.38	970.2	1.031
6.85	1592	.6281	47.59	900.3	1.111
7.59	1607	.6223	49.03	861.5	1.161
8.68	1613	.6200	51.32	805.3	1.242
10.22	1624	.6158	53.40	766.5	1.305
11.54	1645	.6079	55.94	706.3	1.416
13.10	1673	.5977	58.10	673.3	1.485
14.81	1713	.5838	60.23	648.7	1.542
16.76	1775	.5634	62.28	623.6	1.604
17.85	1811	.5522	63.28	613.9	1.629
18.88	1847	.5414	64.30	600.0	1.667
20.11	1907	.5244	65.31	589.8	1.695
21.16	1952	.5123	66.59	577.1	1.733
22.14	2010	.4975	67.62	569.7	1.755
23.13	2059	.4857	68.76	558.8	1.790
24.16	2128	.4699	70.30	542.6	1.843
25.26	2213	.4519	71.83	527.9	1.894
26.27	2300	.4348	73.82	512.9	1.950
27.30	2396	.4174	75.80	496.4	2.015
28.56	2491	.4014	77.83	478.4	2.090
29.95	2375	.4211	79.84	467.6	2.139
30.96	2167	.4615	81.71	454.3	2.201
32.15	1955	.5115	83.69	441.6	2.264
33.50	1757	.5692	85.66	429.9	2.326
34.49	1642	.6090			
35.59	1526	.6553			
36.93	1406	.7112			



Table 12. Temperature dependence of the paramagnetic susceptibility of the Nd-Y  $\delta$ -phase alloy (79.11 wt. % Nd); field strength = 2200 oersteds

T, °K	$\chi_g(\text{theo}) \times 10^6$	$\chi_g^* \times 10^6$	$\frac{1}{\chi_g^*} \times 10^{-4}$	$\mu_{\text{eff}}(\text{Nd})$
50.00	180.1			
77.66		97.39	1.027	3.81
77.73		97.99	1.021	
83.66		96.36	1.038	
86.52		93.72	1.067	
94.40		86.56	1.155	
100.0	90.29			
101.0		82.63	1.210	3.88
106.9		77.15	1.296	
114.3		74.93	1.335	
120.3		68.80	1.453	
124.5		66.74	1.498	3.81
128.7		64.52	1.550	
142.0		60.79	1.645	
146.8		58.82	1.700	3.82
150.0	60.34			
155.6		55.99	1.786	
163.5		53.51	1.869	
168.0		52.27	1.913	
172.1		51.05	1.959	3.82
181.3		48.81	2.050	
186.0		47.72	2.096	
190.4		46.75	2.139	
198.0		45.26	2.209	3.83
200.0	45.35			
203.7		44.16	2.264	
213.5		42.33	2.362	
219.6		41.17	2.429	
226.4		40.09	2.494	3.82
232.9		38.71	2.583	
237.3		38.21	2.617	
243.7		37.39	2.675	
250.0	36.38			
255.1		35.78	2.795	3.82

Table 12 (Continued)

T, °K	$\chi_g(\text{theo}) \times 10^6$	$\chi_g^* \times 10^6$	$\frac{1}{\chi_g^*} \times 10^{-4}$	$\mu_{\text{eff}}(\text{Nd})$
258.5		35.27	2.835	
263.9		34.67	2.884	
268.0		34.22	2.922	
275.4		33.43	2.991	3.82
279.2		33.03	3.028	
282.9		32.82	3.047	
300.0	30.37			
301.1		31.49	3.176	3.86

Table 13. Temperature dependence of the paramagnetic susceptibility of the Nd-Y  $\delta$ -phase alloy (79.11 wt. % Nd); zero field measurements

T, °K	$\chi_g^* \times 10^6$	$\frac{1}{\chi_g^*} \times 10^{-3}$	T, °K	$\chi_g^* \times 10^6$	$\frac{1}{\chi_g^*} \times 10^{-3}$
4.2	690.6	1.448	37.38	273.1	3.662
5.57	554.6	1.803	38.62	232.8	4.296
6.27	513.9	1.946	40.83	209.4	4.776
7.45	434.0	2.304	42.79	189.1	5.288
8.56	374.4	2.671	44.69	181.2	5.519
9.18	385.6	2.593	46.55	170.2	5.875
10.00	343.5	2.911	48.38	166.8	5.995
10.87	324.3	3.084	50.17	159.7	6.262
11.60	316.4	3.161	52.28	152.9	6.540
12.57	299.4	3.340	54.34	150.3	6.653
13.47	288.9	3.461	56.37	143.9	6.949
14.33	281.8	3.549	60.23	134.8	7.418
16.33	269.7	3.708	63.40	126.5	7.905
18.15	260.3	3.842	65.62	122.0	8.197
19.86	255.4	3.915	67.50	117.9	8.482
21.75	251.3	3.979	69.36	107.3	9.320
23.52	254.3	3.932	72.43	106.2	9.416
24.65	255.4	3.915	75.45	106.6	9.381
25.73	259.5	3.854	78.44	95.63	10.46
27.30	267.1	3.744	82.56	97.52	10.25
29.79	652.8	1.532	84.31	94.50	10.58
31.00	604.9	1.653	87.20	90.81	11.01
32.60	1095	0.9132	90.07	86.66	11.54
34.39	2067	0.4838	92.90	81.77	12.23
35.69	1080	0.9259	95.71	78.00	12.82
36.54	422.6	2.366	98.51	73.82	13.55

Table 14. Temperature dependence of the paramagnetic susceptibility of the Ce-Y  $\delta$ -phase alloy (66.00 wt. % Ce); field strength - 3500 oersteds

T, °K	$\chi_g(\text{theo}) \times 10^6$	$\chi_g^* \times 10^6$	$\frac{1}{\chi_g^*} \times 10^{-4}$	$\mu_{\text{eff}}(\text{Ce})$	
50.00	76.62				
80.47		29.94	3.340	2.64	
83.91		29.73	3.364		
87.16		29.46	3.394		
92.58		28.53	3.505		
97.52		27.63	3.619		2.70
100.0	38.70				
109.0		25.86	3.867		
115.6		24.75	4.040		
120.5		24.13	4.144		
124.8			23.50	4.255	2.69
128.9		22.83	4.380		
134.9		21.63	4.623		
138.9		21.46	4.660		
142.9		21.12	4.735		
146.7		20.71	4.829		
150.0	26.03				
150.8		20.29	4.929	2.68	
155.2		19.86	5.035		
159.5		19.54	5.118		
164.3			19.18		5.214
169.5		18.74	5.336		2.69
179.9		17.96	5.568		
185.2		17.50	5.714		
190.2		17.22	5.807		
195.7		16.87	5.928		
200.0	19.69				
201.1		16.51	6.057	2.69	
206.1		16.26	6.150		
214.7		15.18	6.588		

Table 14 (Continued)

$T, ^\circ K$	$\chi_g(\text{theo}) \times 10^6$	$\chi_g^* \times 10^6$	$\frac{1}{\chi_g^*} \times 10^{-4}$	$\mu_{\text{eff}}(\text{Ce})$
223.4		14.95	6.689	2.67
230.5		15.63	6.835	
235.9		14.41	6.940	
242.4		14.12	7.082	
250.0	15.86			
250.6		13.74	7.278	2.68
255.6		13.51	7.402	
261.0		13.28	7.530	
267.6		13.04	7.669	
275.2		12.79	7.819	2.68
281.0		12.66	7.899	
286.6		12.37	8.084	
292.9		12.14	8.237	
300.0	13.34			
300.6		11.73	8.525	2.67

Table 15. Temperature dependence of the paramagnetic susceptibility of the Ce-Y  $\delta$ -phase alloy (66.00 wt. % Ce); zero field measurements

T, °K	$\chi_g^* \times 10^6$	$\frac{1}{\chi_g^*} \times 10^{-3}$	T, °K	$\chi_g^* \times 10^6$	$\frac{1}{\chi_g^*} \times 10^{-3}$
4.2	286.7	3.488	31.79	90.87	11.00
5.06	282.9	3.817	33.60	91.77	10.90
5.89	225.3	4.439	35.36	90.46	11.05
6.50	220.9	4.527	37.06	90.46	11.05
7.30	204.4	4.892	38.72	87.78	11.39
8.30	184.0	5.435	40.93	84.27	11.87
8.94	175.1	5.711	42.89	82.89	12.06
9.41	173.8	5.754	44.79	82.48	12.12
10.22	164.5	6.079	47.38	81.17	12.32
10.87	152.6	6.553	50.09	78.00	12.82
11.79	146.4	6.831	52.89	76.45	13.08
12.84	137.9	7.252	55.62	75.39	13.26
13.82	133.5	7.491	58.30	73.26	13.65
14.91	128.6	7.776	60.92	71.84	13.92
16.11	122.4	8.824	63.49	70.22	14.24
17.23	116.6	8.576	66.00	69.62	14.36
18.64	110.4	9.058	68.53	68.29	14.64
20.00	108.2	9.242	71.00	67.85	14.74
21.57	105.1	9.515	73.44	64.74	15.45
23.07	99.76	10.02	75.85	62.97	15.88
24.77	94.46	10.59			
26.38	91.36	10.95			
27.93	90.87	11.00			
30.13	89.16	11.21			

Table 16. Field dependence of the paramagnetic susceptibility of the alloys investigated;  
 $T = 300^{\circ}\text{K}$

H, oersteds	$\chi_g \times 10^6$	H, oersteds	$\chi_g \times 10^6$
	<u>La-Gd</u>		<u>Nd-Tm</u>
3087.3	168.9	8036.0	70.74
2430.4	169.8	6382.1	70.47
1840.5	170.8	4893.5	70.38
1261.9	171.1	3707.9	70.86
		2981.0	70.98
		2483.5	70.59
	<u>Nd-Y</u>		<u>Ce-Y</u>
6281.6	30.27	8016.7	10.27
4457.0	30.64	6708.5	10.24
3006.4	30.43	5457.8	10.25
2195.5	30.56	4394.2	10.27
		3508.3	10.29

Figure 4. Inverse paramagnetic susceptibility versus temperature curve for  
Mohr's salt, from 77 - 300°K



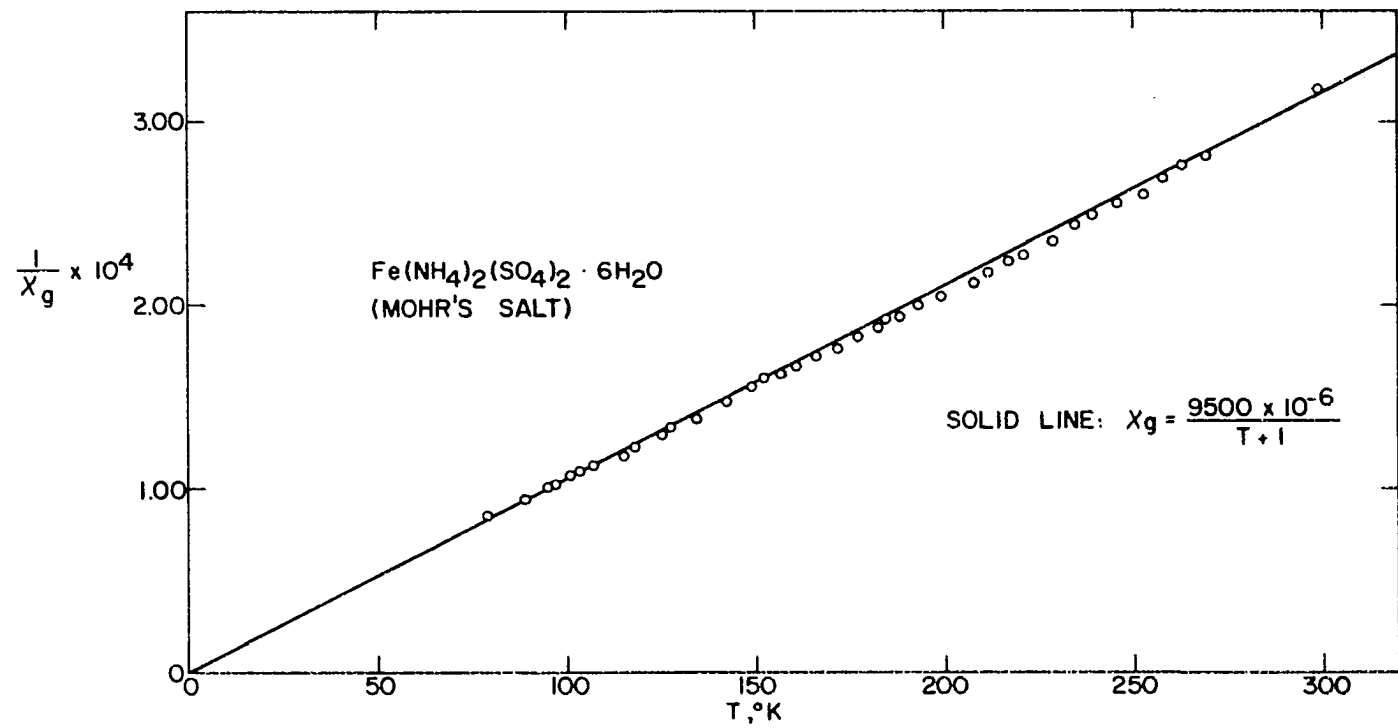


Figure 5. Inverse paramagnetic susceptibility versus temperature curve for La-Gd  $\delta$ -phase alloy, from 4.2 - 300°K

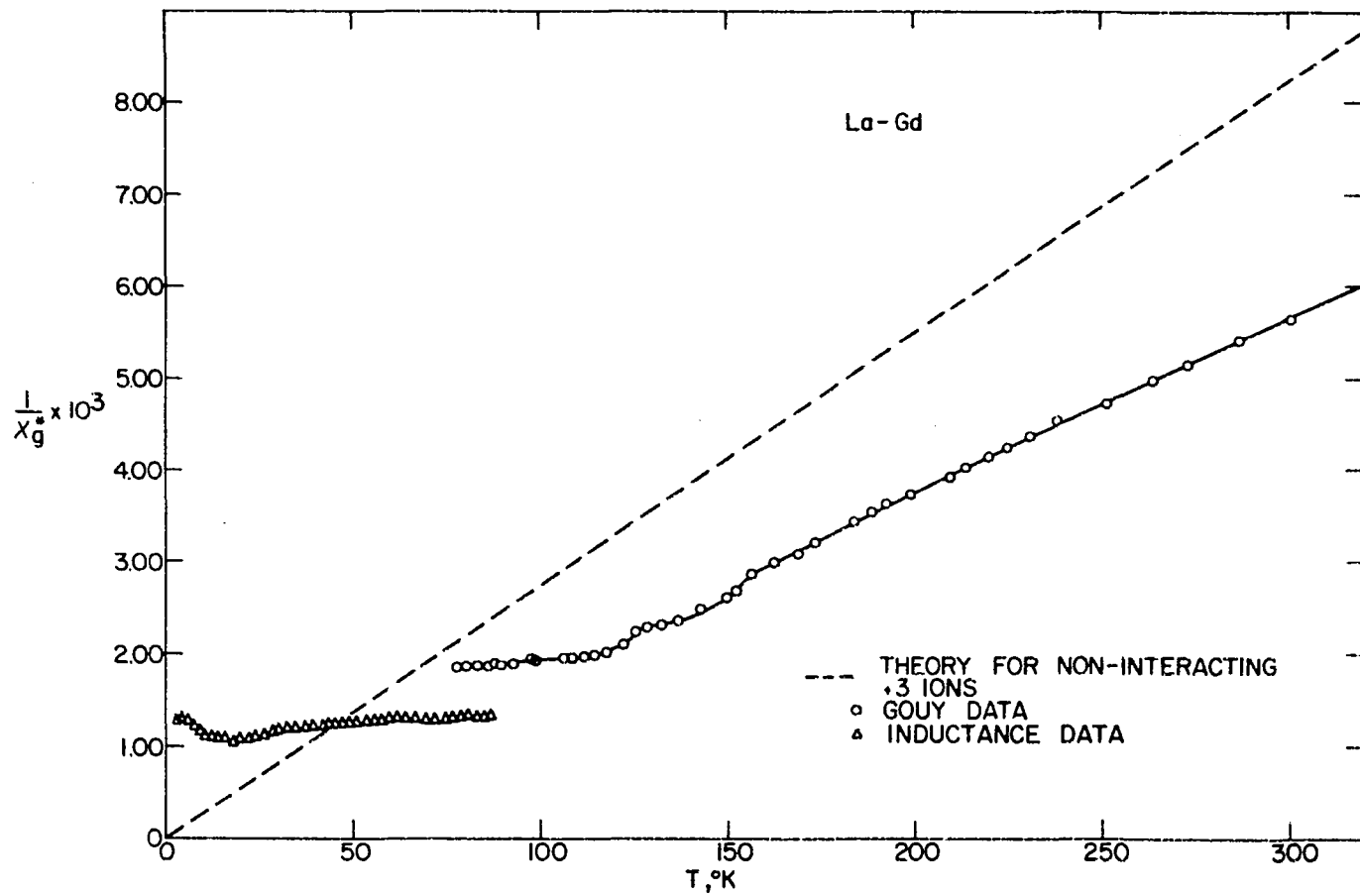


Figure 6. Inverse paramagnetic susceptibility versus temperature curve for La-Gd  $\delta$ -phase alloy, from 4.2 - 100oK

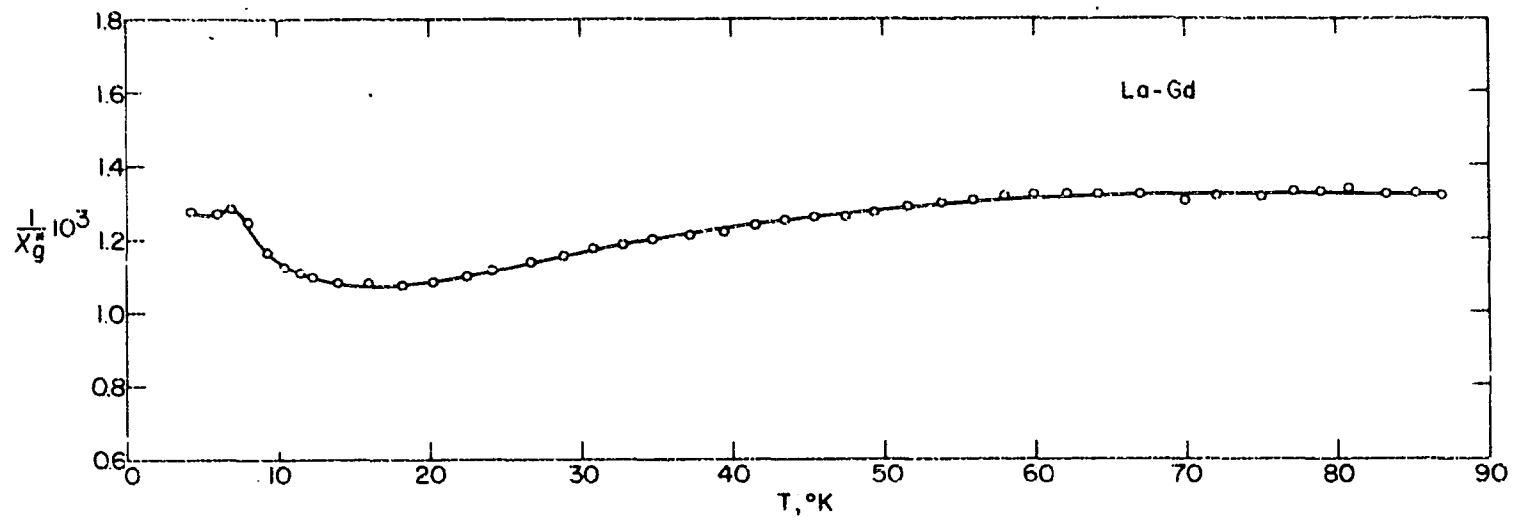


Figure 7. Inverse paramagnetic susceptibility versus temperature curve for Nd-Y  $\delta$ -phase alloy, from 4.2 - 300°K

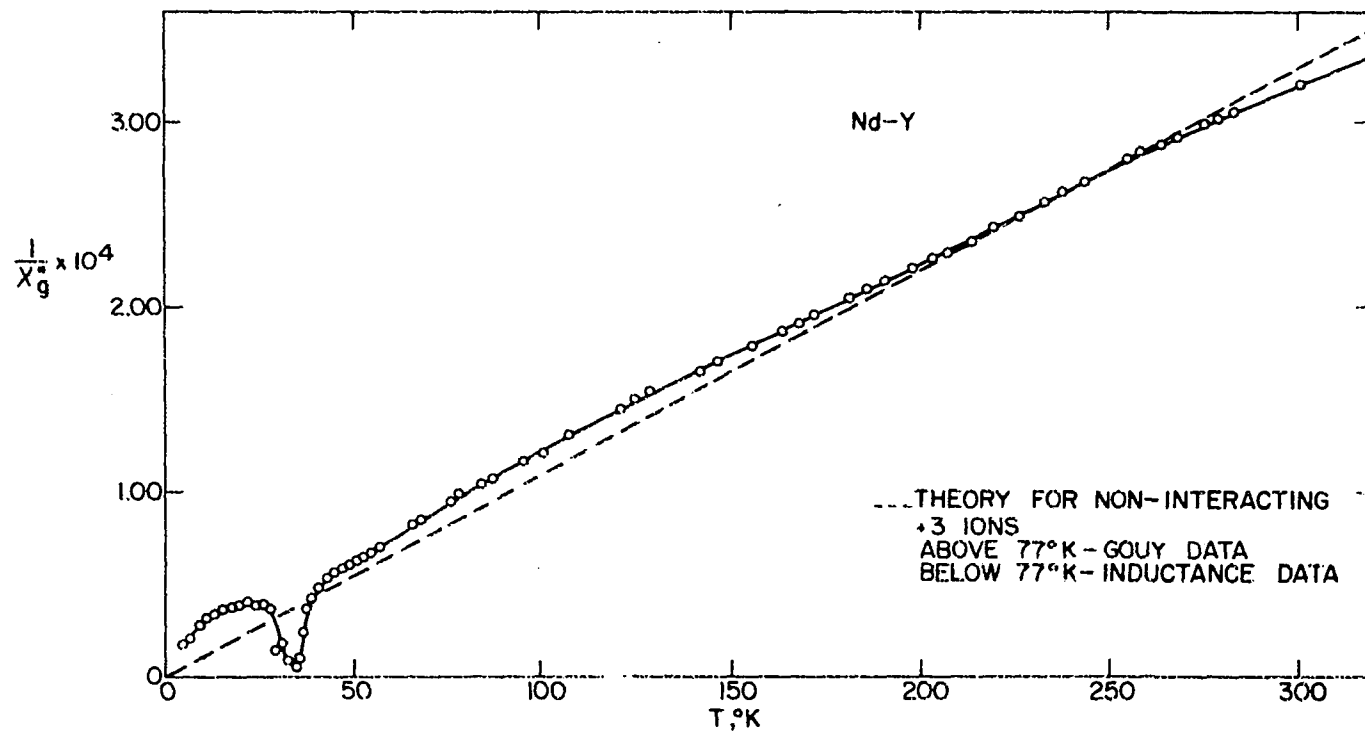


Figure 8. Inverse paramagnetic susceptibility versus temperature curve for Nd-Y  $\delta$ -phase alloy, from 4.2 - 80°K



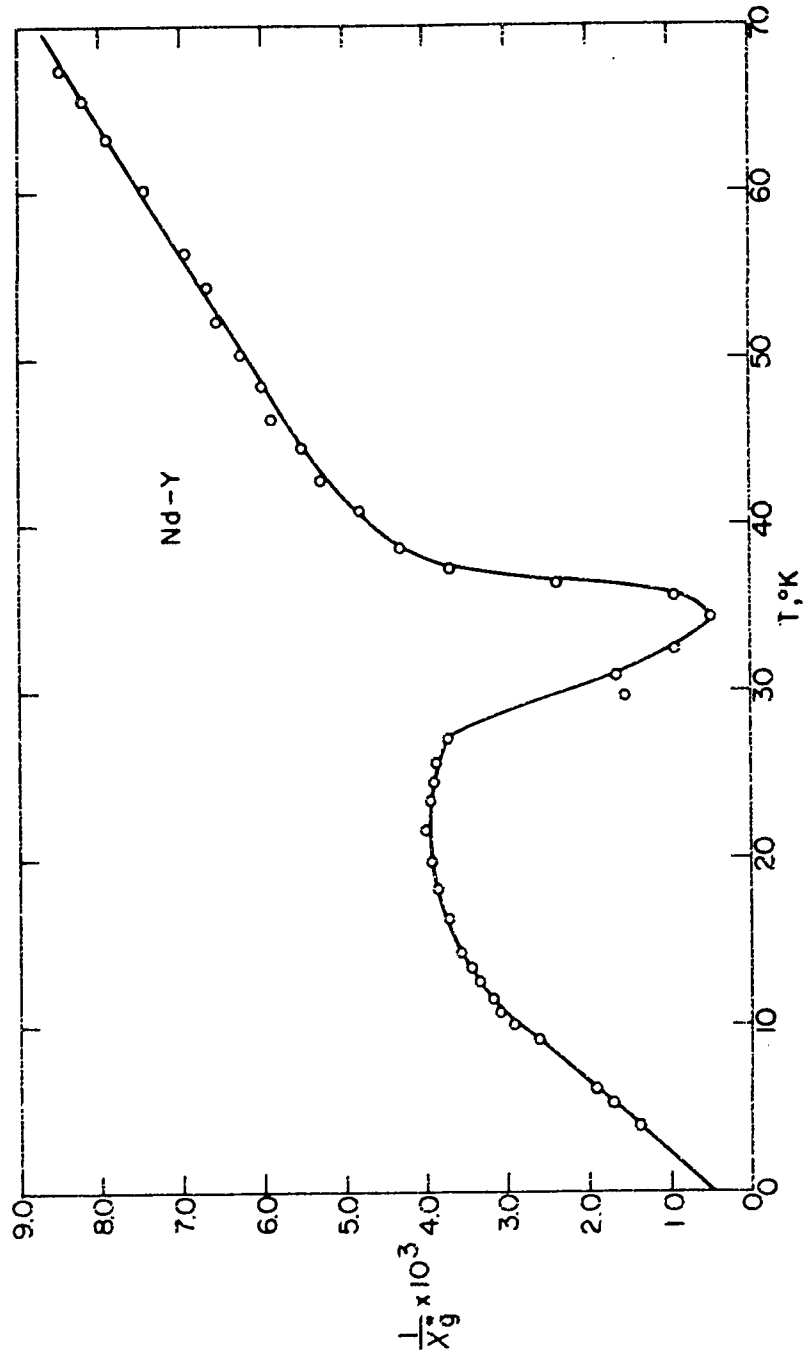


Figure 9. Inverse paramagnetic susceptibility versus temperature curve for Nd-Tm  $\delta$ -phase alloy, from 4.2 - 300°K

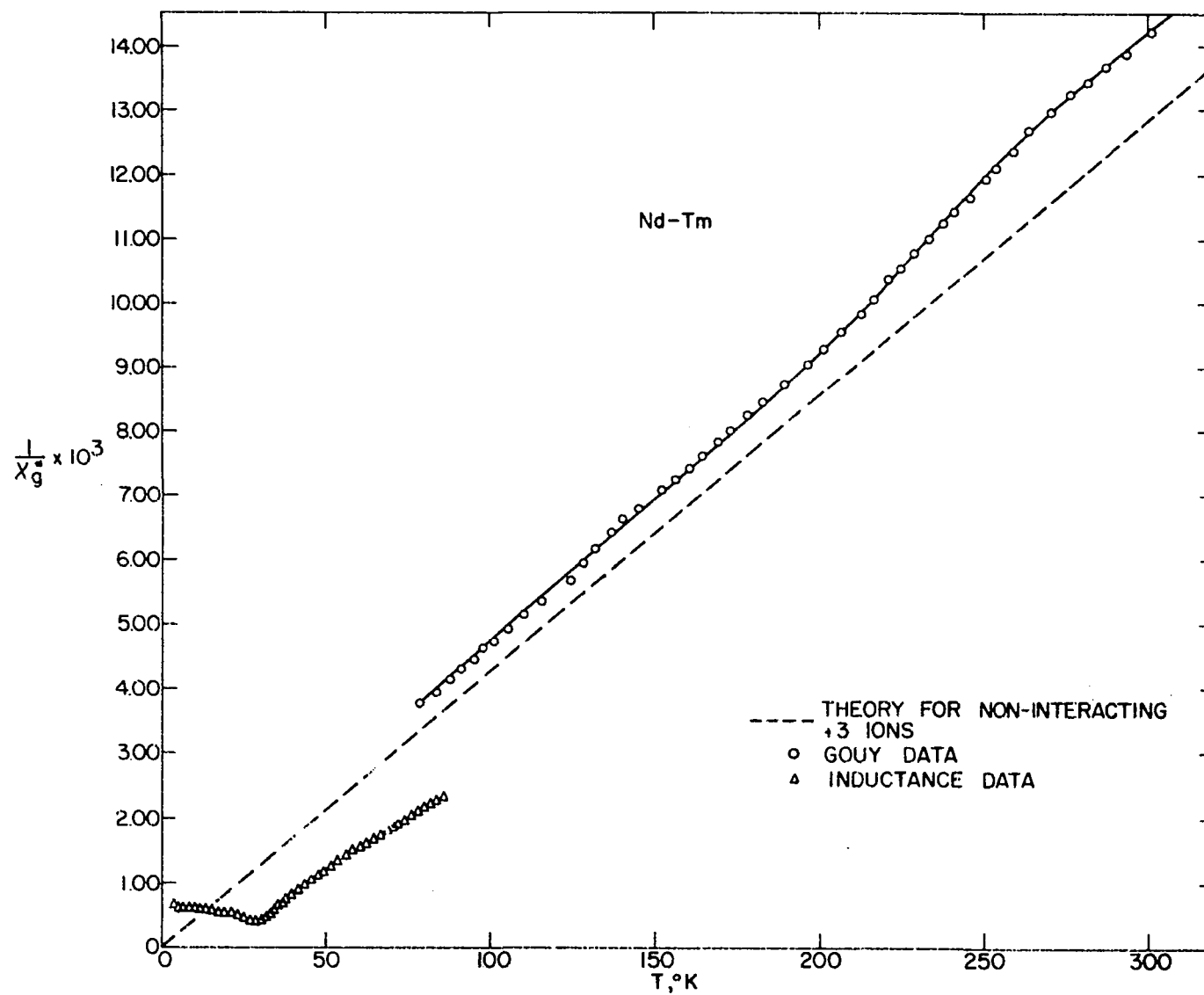


Figure 10. Inverse paramagnetic susceptibility versus temperature curve for Nd-Tm  $\delta$ -phase alloy, from 4.2 - 80°K

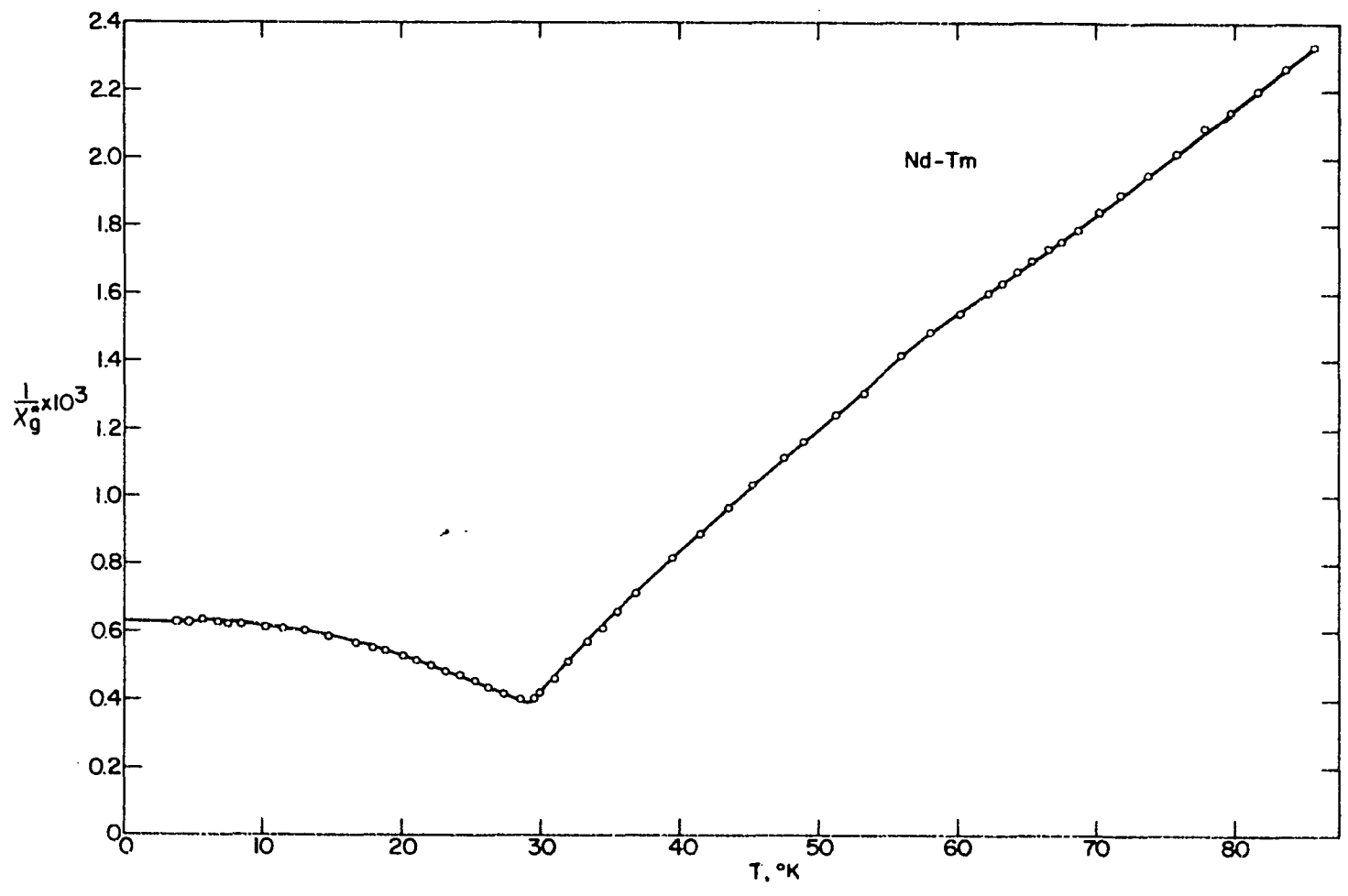


Figure 11. Inverse paramagnetic susceptibility versus temperature curve for Ce-Y  $\delta$ -phase alloy, from 4.2 - 300°K

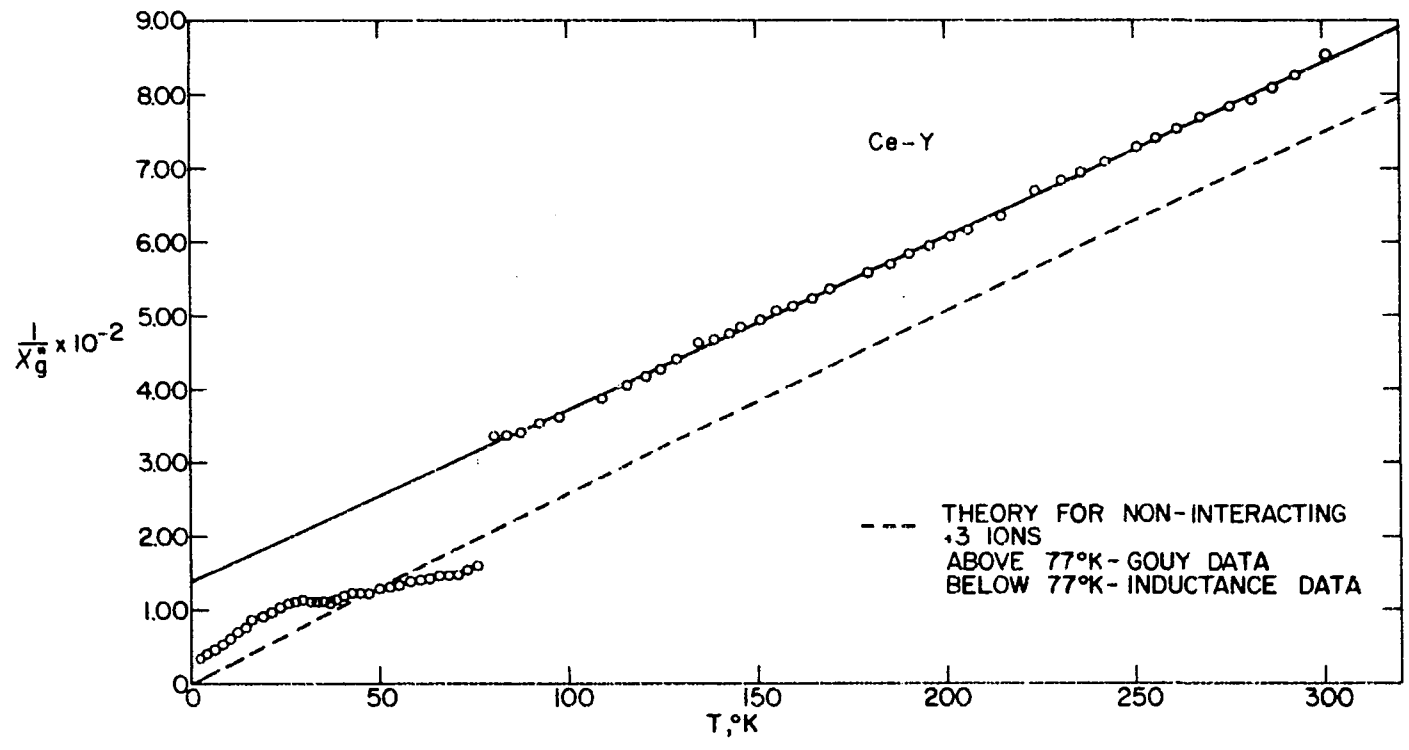
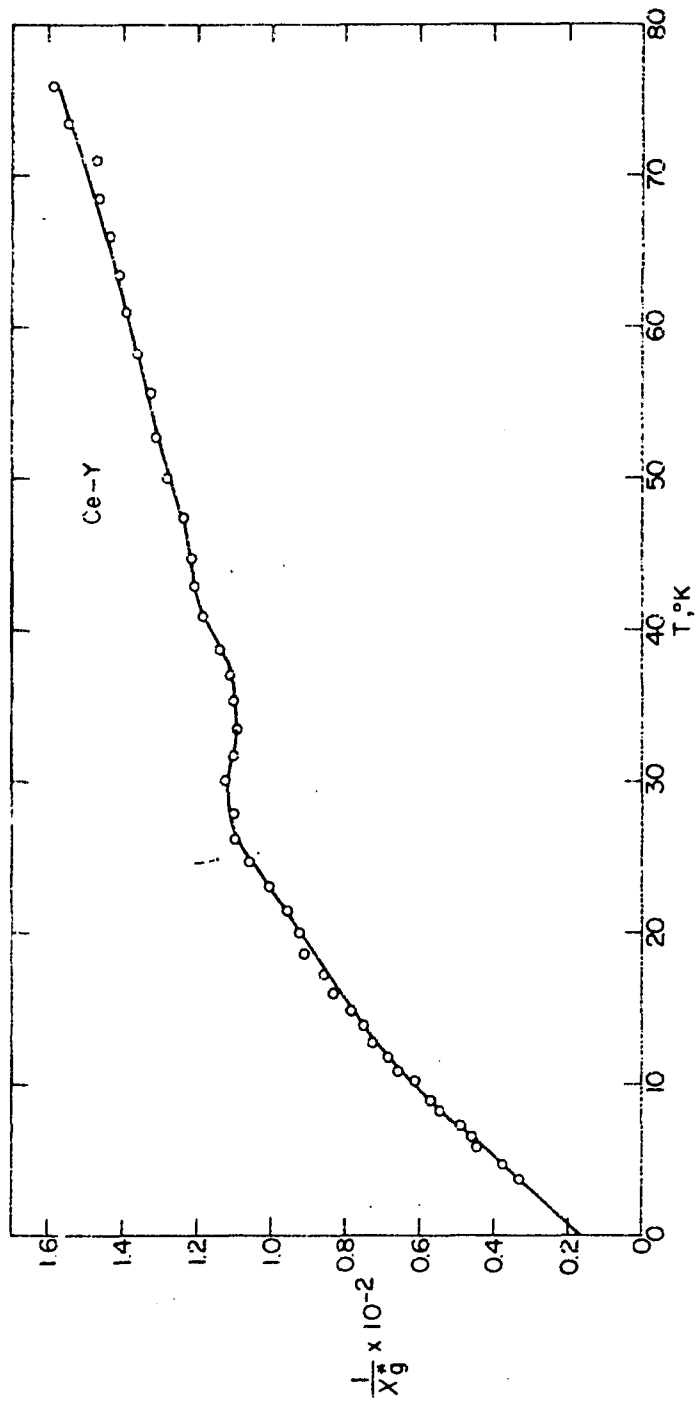


Figure 12. Inverse paramagnetic susceptibility versus temperature curve for Ce-Y  $\delta$ -phase alloy, from 4.2 - 80°K





## V. DISCUSSION

The results presented in the previous section will be summarized at this point, as follows:

1. La-Gd: This alloy consisted of 30.1 atomic percent light, diamagnetic rare earth, and 69.9 atomic percent heavy, paramagnetic. A Curie-Weiss law was obeyed over the temperature range 300 - 155°K., with  $\theta_p = + 10^\circ$ . The susceptibility in this region was higher than that expected from theory, as were the values for the effective magnetic moment of the gadolinium in the alloy. From 130 - 7°K., the susceptibility remained roughly constant.
2. Nd-Y: This alloy was composed of 70.0 atomic percent light, paramagnetic rare earth, and 30.0 atomic percent heavy, diamagnetic. Good agreement was obtained between the observed and theoretical values of the susceptibility from 300 - ca. 40°K., with  $\theta_p = - 24^\circ$ , although the effective moment of the neodymium in the alloy was slightly larger than the theoretical value. A maximum was observed in the susceptibility at 34.5°K.
3. Nd-Tm: In this case, the alloy was made up of two paramagnetic rare earth metals, 63.0 atomic percent of the light, and 37.0 atomic percent of the heavy. A Curie-Weiss relationship was obeyed from 300 - ca. 30°K., with  $\theta_p = - 8^\circ$ , and a susceptibility lower than the theoretical

value. The effective moment calculated for the  $\text{Nd}^{+3}$  ion was slightly higher, and that for the  $\text{Tm}^{+3}$  ion slightly lower, than those expected for the normal tripositive ions. A maximum was observed in the susceptibility at  $28.5^\circ\text{K}$ .

4. Ce-Y: This alloy was of the same general type as the Nd-Y alloy, containing 55.0 atomic percent light, paramagnetic rare earth, and 45.0 atomic percent heavy, diamagnetic. Again a Curie-Weiss relationship was found, from  $300 - \text{ca. } 50^\circ\text{K}$ ., with  $\theta_p = - 57^\circ$ . The observed susceptibility of the alloy was lower than the theoretical susceptibility, while the effective moment of the cerium was slightly higher than the theoretical value. A rather poorly defined region of constant susceptibility appeared to be present from  $26 - 37^\circ\text{K}$ . It should be mentioned that the data obtained for this alloy by the inductance technique are not as accurate as those obtained for the other three alloys, especially at the higher temperatures ( $50 - 77^\circ\text{K}$ .). Over this range, because of the combination of small sample size and small moment, mutual inductance changes were of the order of one turn for this alloy, whereas the other alloys exhibited  $\Delta M$  values at least five times as large. Since the  $\Delta M$  values are obtained from the difference between two large numbers (ca. 30 turns), the degree of accuracy suffers when this

difference is small.

The susceptibilities measured for the Nd-Y and Nd-Tm alloys agree quite well with the theoretical values, although in the latter case, the data is consistently low by approximately 7%. However, marked deviations were observed for the La-Gd and Ce-Y alloys. In the case of the latter alloy, one might expect that the decreased susceptibility was due to the  $Ce^{+3} - Ce^{+4}$  transition. Gschneidner (1961) reports that the valence for  $\gamma$ -Ce, the room temperature form, is 3.1, while that of  $\alpha$ -Ce, the lowest temperature form, is 3.7, and McHargue et al. (1957) have found that only  $\alpha$ -Ce exists at 4.2°K. If one assumes that this transition is the cause of the susceptibility decrease, one can calculate the percentage of  $Ce^{+3}$  present in the alloy at various temperatures from the susceptibility data obtained in this investigation. The results are shown in the following table:

Table 17. Extent of the  $Ce^{+3} - Ce^{+4}$  transition in the Ce-Y  $\delta$ -phase alloy

T, °K	$\chi_g \times 10^6$ (theo. for +3 ion)	$\chi_g \times 10^6$ (obs)	%Ce <sup>+3</sup>	Valence
300	13.34	11.81	88.5	3.12
250	15.86	13.81	87.1	3.13
200	19.69	16.71	84.9	3.15
150	26.03	20.49	78.7	3.21
100	38.70	27.41	70.8	3.29

If this mechanism is responsible for the observed susceptibility, it becomes difficult to explain why the effective moment for the cerium in the alloy exhibits a value of approximately 2.7 Bohr magnetons. The theoretical value for the  $Ce^{+3}$  ion is 2.56, and that for the  $Ce^{+4}$  ion would be zero, so one would expect the moment to decrease with decreasing temperature. The calculated moments for all of the alloys investigated, however, are appreciably higher than the theoretical values, an observation which has been made in all previous studies of intra-rare earth alloys. Thus the above mechanism could be the correct explanation, despite the existence of the high moment, since the increased moment due to alloying might compensate the decreased moment caused by the  $Ce^{+3} - Ce^{+4}$  transition.

The high values of the susceptibility exhibited by the La-Gd alloy are quite difficult to interpret. Thoburn et al. (1958b) found, in a 75 atomic percent Gd alloy, that  $\mu_{eff}(Gd) = 8.38$  Bohr magnetons, and attributed the increased moment to either orbital contributions or transfers from the conduction-band electrons. The present investigation shows an even higher moment, approximately 9.4 Bohr magnetons, and a susceptibility which varies from 37% to 51% above theoretical values. An interesting observation can be made, if one assumes that a conduction electron could somehow be transferred into the 4f shell of gadolinium, resulting in a

${}^7F_6$ , or  $Tb^{+3}$  electronic configuration. Comparison between the observed susceptibility values and those which would be predicted from theory for such a mechanism shows very good agreement, as can be seen from the following table:

Table 18. Comparison between observed susceptibilities of the La-Gd  $\delta$ -phase alloy with those for the  $Tb^{+3}$  ion

T, °K	$\chi_g \times 10^6$ (theo. for 72.46 wt. % $Tb^{+3}$ )	$\chi_g \times 10^6$ (obs)
300.4	179.4	166.8
273.2	197.3	194.1
251.6	214.2	210.2
225.2	239.3	234.6
199.1	270.7	265.0
173.4	310.8	313.7

In addition, it should be pointed out that the theoretical value of  $\mu_{\text{eff}}$  for the  $Tb^{+3}$  ion is 9.72 Bohr magnetons.

In order to explain the magnetic transitions observed in these alloys, we shall have recourse to the theory of antiferromagnetism as developed by Neel (1936) and Van Vleck (1941). There exists a general tendency, in an antiferromagnetic substance, for the atomic moments to line up in an antiparallel array, perpendicular to the direction of the

applied field. Such an alignment gives rise to a temperature-independent susceptibility, since the moments are not free to move with respect to each other. This tendency is opposed by the anisotropic crystalline field, which tends to align the moments in a preferred direction in the crystal. When the applied field is parallel to such a direction, the susceptibility should fall as the temperature is lowered, tending to zero at 0°K. In a polycrystalline sample, however, one must assume that this internal field is randomly oriented. Thus it is perpendicular to the applied field 2/3 of the time and parallel to the applied field 1/3 of the time. It is the combination of these two aligning tendencies in a polycrystalline substance which gives rise to the maximum in susceptibility normally associated with antiferromagnetism.

As a corollary to this theory, one can consider the behavior of a polycrystalline sample of an antiferromagnetic substance as follows: at temperatures close to 0°K., assuming a random distribution of crystal axes, there should be an average susceptibility, given by

$$\bar{\chi}_0 = \frac{2}{3} \chi_{\perp,0} + \frac{1}{3} \chi_{\parallel,0} = \frac{2}{3} \chi_{\perp,0} = \frac{2}{3} \chi_{T_N}$$

since  $\chi_{\parallel} = 0$ . Thus the ratio of the average susceptibility at  $T = 0$  to the susceptibility at  $T = T_N$  should be 2/3.

Applying the theory to the experimental results of

this investigation, we find that maxima occur in the susceptibilities of the Nd-Tm and Nd-Y alloys, suggesting that appreciable anisotropic crystalline fields exist, and that the susceptibility ratios are

$$\begin{aligned}\chi_0/\chi_{T_N} &= 1430 \times 10^{-6}/2070 \times 10^{-6} = 0.69 \text{ for Nd-Y} \\ &= 1540 \times 10^{-6}/2490 \times 10^{-6} = 0.62 \text{ for Nd-Tm}\end{aligned}$$

which are in quite good agreement with the prediction above. The existence of a temperature-independent susceptibility was exhibited by the La-Gd sample, and to a lesser extent by the Ce-Y alloy. Since these alloys are of the same crystal structure as those of Nd-Y and Nd-Tm, the internal fields should be of the same order of magnitude. However, since no maximum occurs in the susceptibilities, one must conclude that the direction of the internal fields in these cases are such as to align the moments perpendicular to the applied field, and that there is little or no tendency for any of the moments to align parallel to the external field. Thus, although antiferromagnetic ordering does occur in these alloys, its direction is free to orient itself perpendicular to the applied field, and hence a temperature independent susceptibility is exhibited.

Concerning the fact that the  $1/\chi$  vs.  $T$  curves obtained from the Gouy data and the inductance data do not coincide,



the following remarks should be made: first of all, as the magnetic data indicate, internal crystalline fields do exist in these alloys. In general, when such a field acts upon an atomic array, a Stark effect takes place, and the field causes a splitting of the atomic levels. In the absence of such an internal field, a large number of atoms are all in a particular energy state, characterized by a certain  $J$  value; when a magnetic field is applied,  $2J + 1$  energy states are established, and the average magnetic susceptibility is determined by the distribution of the atoms in the several states. In the presence of an anisotropic crystalline field strong enough to remove the degeneracy of the level, the level splits into  $2J + 1$  states. Now the separation of these states depends upon the magnitude of the internal field, which is strong or weak, depending on whether the splitting is large or small compared to the multiplet separation. There thus results a redistribution of the magnetic moment which may markedly affect the temperature variation of the susceptibility, especially at low temperatures.

Secondly, the discrepancy could be due to a field-dependent susceptibility. Although field-dependence data obtained for the samples used in the Gouy measurements afforded negative results, it should be remembered that for these measurements, the field was varied from approximately 1000 to 7500 oersteds, i.e., a factor of about 7, while the

field employed in the inductance measurements (ca. two oersteds) was of the order of thousands of times smaller. It is possible that such an extreme variation in field strength would affect the magnitude of the measured susceptibilities to some extent, particularly in view of the remarks made in the preceding paragraph. Finally, the observed deviations could have arisen from the fact that the samples used in the inductance measurements were not truly spherical, as was mentioned in a preceding section. Thus, demagnetization effects larger than those associated with a perfect sphere could contribute to the susceptibility values. In any case, the general shapes of the  $1/\chi$  vs.  $T$  curves were reproduced in the temperature regions in which data from both techniques were available.

There are many avenues along which further research with alloys of the type investigated in this work should be conducted. Suggestions as to the nature and magnitude of the internal crystalline fields present could be obtained from single crystal structural studies. In conjunction with such studies, although the data obtained in the present investigation do not give a clear-cut distinction between the three types of  $\delta$ -phase alloys, resistivity measurements should be carried out to determine if any indication of atomic ordering is present, i.e., whether or not the atoms tend to occupy preferred sites in the crystal. Susceptibility measurements

on single crystals at low temperatures would allow one to separate the average susceptibility into  $\chi_{\perp}$  and  $\chi_{\parallel}$  components, thus affording quantitative data on the distinction between the two types of behavior observed in the susceptibilities below the Néel points. In relation to this point, low temperature heat capacity measurements could also shed some light on this dissimilarity. Finally, nuclear magnetic and paramagnetic resonance studies on these alloys should afford interesting data, particularly in the case of the La-Gd alloy, where such studies would determine whether or not the gadolinium in this alloy has assumed the  $7F_6$  configuration, as the magnetic data appear to indicate.

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