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**RARE EARTH-MANGANESE ALLOYS, THEIR PREPARATION,
CRYSTAL STRUCTURES, PHASE DIAGRAMS,
AND MAGNETIC PROPERTIES**

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TECHNICAL REPORT AFML-TR-66-366

JANUARY 1967

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ABSTRACT

The compounds and alloys between rare earth (RE) metals and manganese have been studied systematically. For the preparation of these alloys a special technique has been developed, the so-called "amalgam process," which consists of a heat treatment of an RE-Me-amalgam, where RE can be any RE metal and Me any other metal. The process yields mercury-free, well-annealed compounds without a melting process at temperatures between 800° to 1100°C. On thus prepared RE-Mn alloys the crystal structures of the intermetallic compounds with the formulas $RE Mn_2$, $RE_6 Mn_{23}$, and $RE Mn_{12}$ have been determined to be of the $MgCu_2$ or $MgZn_2$, $Th_6 Mn_{23}$, or $Th Mn_{12}$ type, respectively. The phase diagrams of the RE-Mn system (RE = Gd, Dy, Ho, Er) have been established mainly by differential thermal analysis. All of these intermetallic compounds are formed peritectically. The magnetic properties of the intermetallic compounds present in the investigated systems have been determined in the temperature range 80° to 1400°K. The magnetization, saturation magnetization, and susceptibility as well as the Curie points and magnetic moments have been established. Various modes of ferrimagnetic coupling of the moments are observed. A mechanism is proposed which can explain the experimental results and is consistent with theoretical considerations.

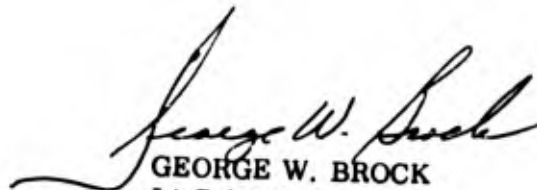
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FOREWORD

This report was prepared by Prof. Dr. Franz Lihl and Dr. Hans R. Kirchmayr, both of the Institute of Technology (Dept. of Applied Physics), Vienna, Austria. The work reported was sponsored by the Air Force Materials Laboratory, Research and Technology Division, under Contract AF61(052)-609. This contract is carried under Project 7367, "Research on the Characterization and Properties of Materials," Task 736703, "Electronic and Magnetic Properties of Materials." It was administered under the direction of project engineer Dr. K. Strnat of the Materials Physics Division, Air Force Materials Laboratory.

The research reported in this document was sponsored through the European Office of Aerospace Research. The work reported was accomplished between 1 April 1962 and 30 March 1966. The manuscript was released in November 1966.

This technical report has been reviewed and is approved.



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SECTION I

INTRODUCTION

The rare-earth (RE) metals (which term includes scandium, yttrium, and the lanthanides) form a unique group of metals of considerable interest to physicists, chemists, and metallurgists. For many years the chemical similarity of these 17 elements has hindered the preparation of pure RE metals which were not contaminated by other RE metals. Now, since the late 1950's, the pure RE metals are commercially available and are produced in ever increasing amounts and at falling prices. On the other hand the chemical similarity is the main reason for the interest of the physicist and metallurgist in these metals because by substituting one RE element for another in a special compound or phase the physical properties are usually altered in a nearly continuous way. Therefore, many series of compounds with the general formula RE_xA_y have been prepared, where RE can be any RE metal or a mixture of two or more RE metals; A may be any element besides the transition metals of Group IV to VI of the periodic table or besides the noble gases, which do not form any compound with RE metals.

Whereas most chemical and physical properties change only slightly if one RE metal is replaced by another, the magnetic properties can change drastically. This is due to the 4-f electrons of the RE metals which are shielded from the outer electrons and therefore contribute little to the chemical and metallurgical properties but dominate the magnetic properties as long as the 4-f shell is unfilled.

The only other group of elements having an unfilled inner shell and therefore bearing a primary magnetic moment are the transition elements, especially the 3-d elements, Mn, Fe, Co, and Ni. It is therefore understandable that alloys and compounds consisting of a combination of 3-d and 4-f metals are likely to possess very complex magnetic properties, which are highly interesting from the practical as well as from the scientific aspect.

Of these metals manganese is a special case. Although not ferromagnetic itself, it is capable of showing ferromagnetic ordering when combined with other metals, especially transition metals. On the other hand, manganese is also a special case in regard to the physical metallurgy of RE-transition metal alloys. Although the elements of Groups IV, V, and VI (Ti, V, Cr, etc.) do not form a single intermetallic compound with the RE metals, it has been found that Mn forms with some RE elements up to 3 intermetallic compounds and that the elements Fe, Co, and Ni form up to 9 intermetallic compounds with all RE elements.

The RE-Mn alloys and compounds are therefore likely to show physical, metallurgical, and magnetic properties which are especially sensitive to slight changes in the electron configuration, the atomic size, etc. In this report the results of systematic investigations of the phases and intermetallic compounds of 10 binary RE-Mn systems are given, which have been chosen from the 17 possible RE-Mn systems by scientific as well as economic considerations.

SECTION II

PREPARATION OF RE-Mn ALLOYS AND COMPOUNDS

CONVENTIONAL METHODS

The preparation of RE-Mn alloys may be achieved by many conventional methods, e.g., arc melting, induction melting, sintering, etc. These preparation techniques, however, have severe limitations. There exists no crucible material which can be used throughout. Only tantalum can be used, but then only to a limited extent because up to 1 wt. percent Ta is soluble in most RE metals (Reference 1). Refractory materials like alumina are usually wetted by the melt, and only pore-free crucibles are suitable to a limited extent. When using crucible-free methods such as arc melting a great deal of the RE metal and of the Mn metal usually evaporates. This is true especially for the RE-metals with a low boiling point, like Sm, Eu, Yb, etc. In either case the composition of the alloy is altered in a way which can not be foreseen. Therefore, single-phase alloys are prepared more or less only by accident. From the phase diagrams of the RE-Mn systems, given in this report, it can be seen that most compounds are formed peritectically. Therefore, by rapid cooling, which takes place when the arc-melting technique or high-frequency induction melting is used, only mixtures of RE-Mn compounds can be achieved.

Most of these difficulties can be overcome by a special technique, developed by our laboratory, called the amalgam process. Consequently, most alloys used for our investigations have been prepared by this process.

THE AMALGAM PROCESS

The scheme of the amalgam process, applied to RE-Mn alloys, is given in Figure 1. It was originally developed by F. Lihl (Reference 2 and 3) for the preparation of alloys and compounds at temperatures below the boiling point of mercury. It has been modified for the preparation (Reference 4, 5, and 6) of RE alloys in general (RE-Mn, -Fe, -Co, -Ni, -Cu, -Ag, -Au, etc.). This modification, requiring a considerable amount of development work, has been necessary since the RE metals form very stable compounds with mercury (Reference 7). Alloys and compounds between RE metals and elements of all groups of the periodic table (besides the noble gases) have been successfully prepared and investigated by the amalgam process. The thermodynamic and theoretical foundation of the amalgam process is given elsewhere (Reference 8). Here, only its application to RE-Mn alloys will be discussed.

Preparation of the RE-Mn Amalgams

The binary systems Mn-Hg and RE-Hg are now reasonably well known. In the system Mn-Hg two intermetallic phases have been detected (Reference 9), namely, MnHg and Mn_2Hg_5 . Mn_2Hg_5 decomposes at 75°C into MnHg and Hg. MnHg decomposes at 400°C into finely divided Mn metal and Hg vapor. The solubility of Mn in liquid Hg is 1×10^{-2} wt. percent at room temperature and 1.5 wt. percent at 450°C (Reference 10).

The RE-Hg systems have been evaluated in the last few years. At least three intermetallic phases are present in each of the systems RE-Hg (RE = Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, and Er), namely, $REHg_3$, $REHg_2$, and REHg (References 11, 12, and 13).

The solubility of the RE metals in liquid mercury is approximately 0.01 wt. percent at room temperature, 1 wt. percent at 450°C (References 14 and 15). The preparation of the

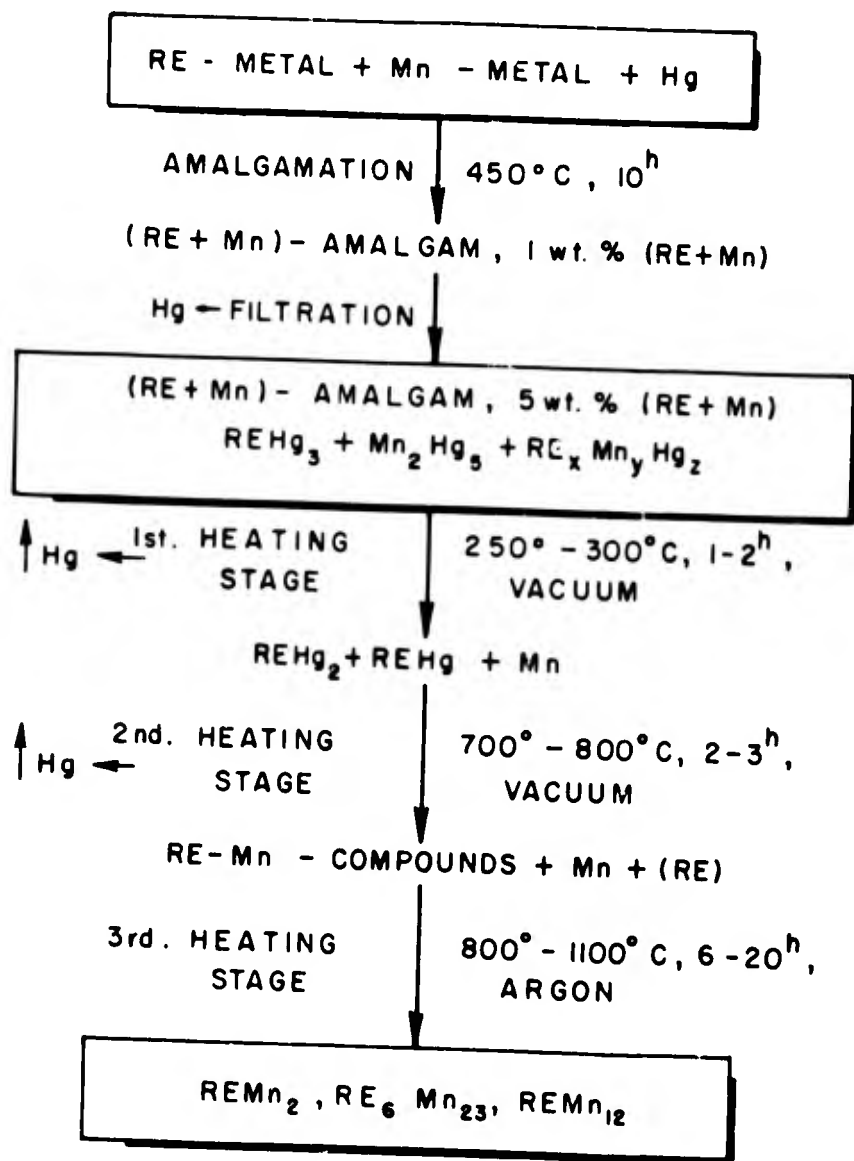


Figure 1. Scheme of the Amalgam Process

RE-Mn amalgams consists of a heating process of a mixture of liquid mercury, RE metal, and Mn metal at 450°C. During the heating process the amalgam, which is kept in argon atmosphere in a fused glass tube, is agitated slowly. The details of the procedure are given elsewhere (References 5, 6, and 11). After cooling, the amalgam consists of RE-Hg and Mn-Hg compounds wetted by liquid mercury. This liquid mercury is filtered off and the residue is a pasty amalgam; it decomposes readily at room temperature under the influence of oxygen, but can be kept without decomposition for weeks at liquid air temperature.

Heat Treatment

The amalgams thus prepared are heat-treated in the manner shown in Figure 1.

The first stage consists of a distillation process, which eliminates the free, unreacted mercury. This process is conducted at the lowest possible temperature to avoid partially dissolving the RE or Mn metal in the liquid mercury. After approximately 1 hour a finely divided intimate mixture of RE-Hg compounds (REHg_3 and REHg_2) with Mn metal grains is achieved.

The second stage consists in the removing of Hg, which is left bound in the alloy. This step necessitates 700° to 800°C and 2 to 3 hours. During this stage either a stream of argon with 5 to 10 Torr pressure or vacuum can be used. The temperature of 700° to 800°C must be approached slowly (approximately within 1 hour). If this temperature is reached too quickly, partial sintering of the alloy occurs, thus preventing the complete removal of the Hg.

Then, in the third and last heating stage, a homogenization of the alloy powders by diffusion takes place. During this step single-phase alloys may be formed, depending on the ratio between the RE metal and the Mn initially used when preparing the RE-Mn amalgam.

Usually 800° to 1100°C and 6 to 20 hours are sufficient to reach equilibrium.

Mechanism

The mechanism of this reaction is as follows: At 500°C the mercury compounds, which are stable at room temperature, have been decomposed into REHg and Mn metal. The Mn grains obviously are separated by the REHg grains, since a growing of the Mn grains can not be observed, even if the alloy is kept at 500° to 600°C for up to 24 hours. When the temperature is raised, the REHg compounds decompose, and obviously the free RE metal immediately reacts with the Mn grains. The Mn grains are therefore covered by shells of RE-Mn compounds. In the last heating stage by a diffusion process, which needs only 6 to 20 hours at 800° to 1100°C, equilibrium is achieved. This short time is sufficient since the diffusion distances are very short. The highest temperature necessary depends on the RE-Mn systems investigated. Usually best results are obtained if this temperature is slightly higher than the eutectic and slightly lower than the peritectic temperatures (see Section IV for the phase diagrams).

SECTION III

CRYSTAL STRUCTURES OF RE-Mn COMPOUNDS

In the RE-Mn systems, three types of intermetallic compounds have been detected, namely, the compounds $RE Mn_2$, $RE_6 Mn_{23}$, and $RE Mn_{12}$.

 $RE Mn_2$ COMPOUNDS

The $RE Mn_2$ compounds have been investigated to some degree earlier (Reference 13). Two types of structures were observed, the cubic $MgCu_2$ - (C15) type and the hexagonal $MgZn_2$ - (C14) type. Table I gives the structures and lattice spacings of our investigations on (Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, and Er)-Mn compounds as well as the data of earlier investigations.

Only a few points will be discussed. In general, the earlier investigations could be confirmed. Also the lattice spacings agree well. The decrease of the lattice spacings of $RE Mn_2$ compounds with increasing atomic number is regular, as can be seen from Figure 2.

There exists a regular change of the structures between the C14- and C15-types. The light RE elements form Laves compounds with the C15 structure; so does yttrium. The heavier elements, beginning with erbium, form the C14 structure. We have found that Ho can form a $Ho Mn_2$ compound with either the C14 or the C15 structure. Usually, when applying arc-melting techniques, the cubic C15 structure is formed. By means of the amalgam process, however, the C14 structure has also been observed. This structure has been confirmed not only by calculating the proper lattice spacings from all diffraction lines, but also by calculating the structure factors and intensities which agreed well with the observed values. We are now studying by high temperature X-ray diffraction techniques, whether this C15 structure is metastable at all temperatures or whether there exists a distinct temperature of transformation for these two structures. In either case, it is reasonable to assume that especially $Ho Mn_2$, which is at the border between the ranges of existence of the C14 and C15 structures, can accept both structures.

 $RE_6 Mn_{23}$ COMPOUNDS

The existence of an intermetallic compound of approximately 80 at. percent Mn in most RE-Mn in most RE-Mn systems has been known for some years. Also some physical, especially magnetic, properties have been reported concerning these compounds (References 18 and 19). The formulas $RE Mn_4$ (RE = Y, Gd, Ho) and $RE Mn_5$ (RE = Y, Gd, Dy, and Ho), as given in References 20, 21, and 22, have also been attributed to these compounds. Only recently has the structure of these compounds been established as the $Th_6 Mn_{23}$ type (References 16 and 17).

Nevertheless there are some questions unanswered: whether these compounds with different formulas are identical, whether such compounds exist in all or only in some RE-Mn systems, and finally, whether there exists a range of homogeneity in the compounds. The results of our investigations may help to clarify some of these questions.

From Table I it can be seen that except for La, Ce, and Pr, all RE elements investigated form $RE_6 Mn_{23}$ compounds. The lattice spacings observed by us agree well with values from other sources. Figure 3 shows the decrease of the lattice spacing, a , with increasing atomic number. This decrease is also regular.

TABLE I

Lattice Spacings and Structures of RE-Mn Compounds (in Å)

	RE ₂ Mn ₂ (C15 or C14 Type)	Ref. No.	RE ₆ Mn ₂₃ (Th ₆ Mn ₂₃ Type)	Ref. No.	RE ₁₂ Mn ₁₂ (ThMn ₁₂ Type)	
	a		a		a	c
Y	7.692 7.679	- 13	12.457 12.438 12.47	- 16	8.595	4.773
La	-		-		-	-
Ce	-		-		-	-
Pr	-		-		-	-
Nd	-		12.663 12.657	- 16	8.660	4.810
Sm	-		12.572 12.558 12.67	- 16 17	-	-
Gd	7.750 7.728	- 13	12.519 12.532 12.51	- 16	8.624	4.782
Dy	7.602 7.569	- 13	12.358 12.361 12.38	- 16 17	8.579	4.763
Ho	7.592 a= 5.368) c= 8.764) 7.507	- - - 13	12.331 12.324 12.34	- 16 17	8.570	4.747
Er	a= 5.307) c= 8.702) a= 5.281 c= 8.621	- - 13 13	12.285 12.275 12.29	- 16 17	8.540	4.740

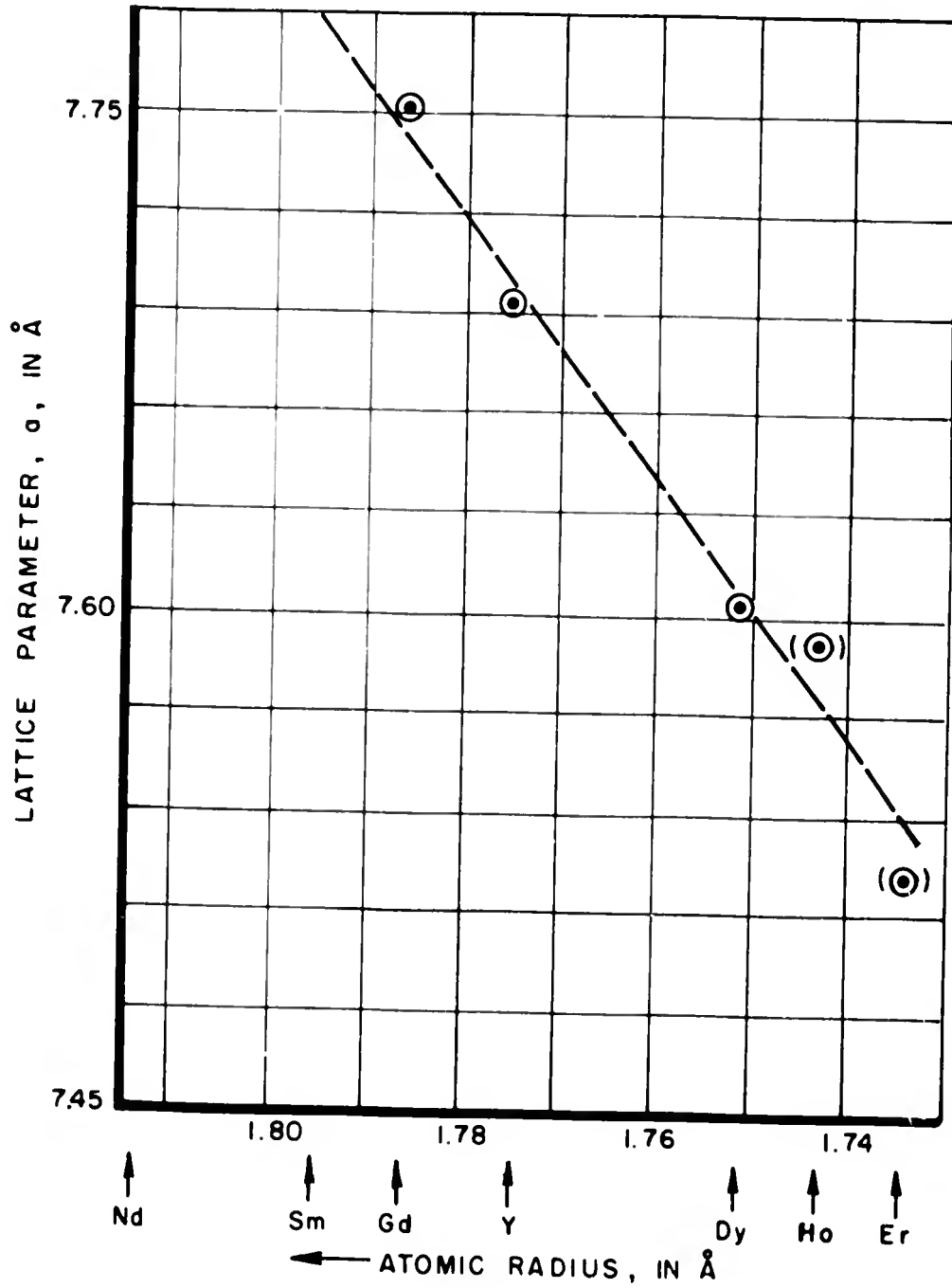


Figure 2. Lattice Spacings of $REMn_2$ Compounds

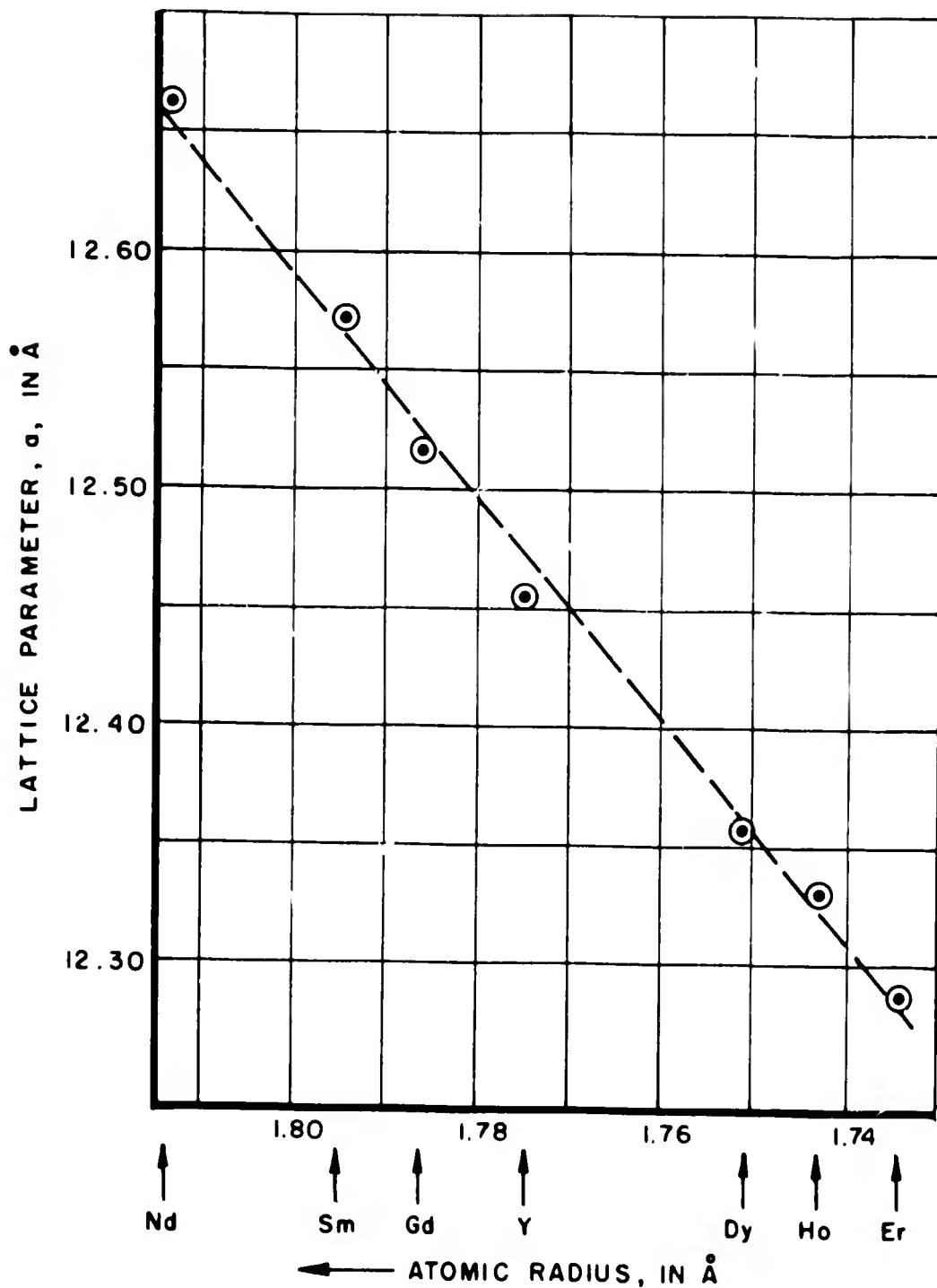


Figure 3. Lattice Spacings of RE₆Mn₂₃ Compounds

The formation of RE_6Mn_{23} compounds has been explained on the basis of a size dominant factor (Reference 16). The nonexistence of La_6Mn_{23} , Ce_6Mn_{23} , and Pr_6Mn_{23} , however, can not be explained by a size factor effect. An explanation has been proposed based on the immiscibility gap observed in these systems (Reference 23), which prevents a complete mixing of the two liquid elements. Since, however, the amalgam process does not necessitate a liquid phase, such a RE_6Mn_{23} compound should form, if it is stable at all. Therefore the systems La-Mn and Ce-Mn have been tested by the amalgam process. As far as our present results indicate, under similar conditions which led to the formation by the amalgam process of other RE_6Mn_{23} compounds, La_6Mn_{23} and Ce_6Mn_{23} could not be prepared. It seems therefore that the immiscibility gap in these systems may indicate the instability of the corresponding compounds rather than the prevention of the formation of such compounds because of mechanical, macroscopic considerations. The same seems to be true with the Pr_6Mn_{23} compound.

The existence or nonexistence of the different compounds reported earlier cannot be proved by crystallographic means alone. By magnetic investigations, however, it has been shown that there exists only one intermetallic compound in the concentration range from 79.5 to 83.3 at. percent Mn in each system. This is based on the fact that the Curie temperatures reported are the same and that also, by differential thermal analysis, only one compound has been detected in this region. These conclusions agree with results of X-ray diffraction investigations, which yielded either patterns which could be indexed entirely on the basis of the RE_6Mn_{23} structure or patterns showing additional lines due only to $RE Mn_2$ or $RE Mn_{12}$ compounds. However, it must be recognized that the compounds RE_6Mn_{23} , $RE Mn_4$ and $RE Mn_5$ differ only slightly in composition (79.5, 80, or 83.3 at. percent Mn, respectively). Such small differences of composition do not allow an accurate distinction of the formulas by chemical analysis of samples regarded as single phase.

In the original paper by Florio et al. (Reference 24), regarding the Th_6Mn_{23} type of structure, the possibility that the actual structure may be Th_6Mn_{24} , corresponding to $Th Mn_4$ (= $RE Mn_4$), was left open. This possibility is regarded as improbable (Reference 16) because of results obtained on $Sr Mg_4$, which has a hexagonal instead of a cubic structure.

Nevertheless, the possibility of a range of homogeneity which covers all or two of the compositions RE_6Mn_{23} , $RE Mn_4$, and $RE Mn_5$ could not be excluded. Therefore careful experiments have been performed on Gd_6Mn_{23} , in which the usual measuring and calculating techniques to obtain lattice spacings with high precision were applied. In all cases, due to the finely grained, well-annealed state of the powders prepared by the amalgam process, a separation of the $K\alpha_1$ and $K\alpha_2$ lines of $CrK\alpha$ radiation, beginning from $2\theta = 90$ degrees, were observed.

By these experiments a marked difference between lattice spacings of samples with the composition $RE Mn_{3,2}$ to $RE Mn_5$ (i.e., from 76 to 83.3 at. percent Mn) could not be observed within a limit of $\pm 0.002 \text{ \AA}$. Also, the intensities of the diffraction lines were found to be in good agreement with calculated intensity data (Reference 25) based on the Gd_6Mn_{23} structure and composition.

Therefore, if a range of homogeneity exists, it must be small, at least in the case of Gd_6Mn_{23} , and this formula must be regarded as an accurate expression of the composition.

REMn₁₂ COMPOUNDS

This group of compounds has been supposed to exist, since the compound YMn₁₂ was characterized earlier (Reference 20), and the compounds GdMn₁₂ and DyMn₁₂ have been reported to exist (Reference 26), but a characterization of their structure has not been given up to now.

We have investigated the systems RE-Mn (RE = Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, and Er) and found in all of these systems besides the systems (La, Ce, Pr, Sm)-Mn that there exists an REMn₁₂ compound. The structure is body-centered tetragonal; the lattice spacings are contained in Table I. Their decrease with increasing atomic number is regular (Figure 4).

Since the compound ThMn₁₂ belongs to the space group 14/mmm the same structure has been tested to determine if it also fits the REMn₁₂ structure. By calculating the structure factors and intensities (Reference 25) and by measuring the intensities at low (90°K) and normal temperature with a low temperature X-ray diffraction goniometer attachment, the structure has been confirmed as identical to the ThMn₁₂ structure. No systematic deviation of the intensities due to free parameters, different from the ThMn₁₂ compound, has been observed. The atoms occupy the following positions:

2 (a) RE at 0,0,0.

8 (f) Mn at $1/4, 1/4, 1/4$; $3/4, 3/4, 1/4$; $1/4, 3/4, 1/4$;
 $3/4, 1/4, 1/4$.

8 (i) Mn at $x, 0, 0$; $\bar{x}, 0, 0$; $0, x, 0$; $0, \bar{x}, 0$; with $x = 0.36$.

8 (j) Mn at $x, 1/2, 0$; $\bar{x}, 1/2, 0$; $1/2, x, 0$; $1/2, \bar{x}, 0$; with $x = 0.28$.

The interatomic distances calculated with these positions seem to be reasonable when compared with the average diameter of the RE atoms and the diameter of the Mn atoms.

Up to now no range of homogeneity has been observed in these compounds.

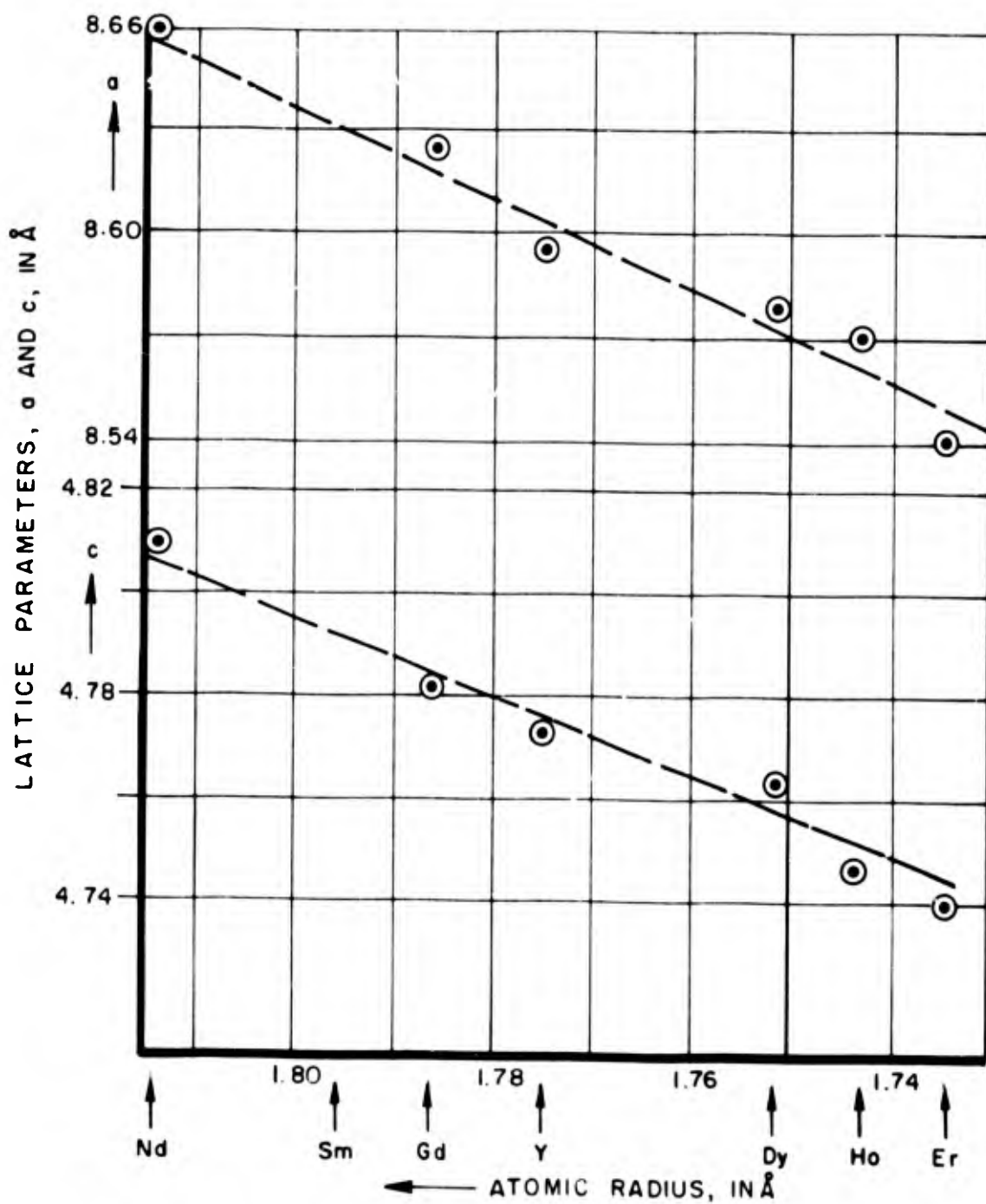


Figure 4. Lattice Spacings of REMn₁₂ Compounds

SECTION IV

RE-Mn PHASE DIAGRAMS

LITERATURE SURVEY

The phase diagrams of the RE-transition metal systems, especially with Mn, Fe, Co, and Ni, are not well investigated. There are numerous intermetallic phases existing in these systems (References 13 and 23), but complete phase diagrams are scarce. A recent compilation (Reference 27) shows that from the 204 possible binary systems between the 17 RE metals and the elements of Groups VII and VIII, which form at all intermetallic compounds, only 19 complete phase diagrams exist in the following combinations:

Mn-Y, -La, -Ce
 Fe-Y, -La, -Ce, -Nd, -Gd
 Co-Y, -Ce, -Gd, -Dy
 Ni-Y, -La, -Ce, -Pr, -Nd
 Ru-Ce
 Re-Y

Since at least a limited knowledge concerning the phase diagrams is essential, the phase diagrams of the systems Gd-Mn, Dy-Mn, Ho-Mn, and Er-Mn have been investigated, mainly by DTA methods. The preparation of the alloys has usually been performed by the amalgam process. The chemical composition has been determined by X-ray fluorescence analysis (Reference 28).

MEASURING TECHNIQUE

The usual arrangement of the differential thermal analysis, (a combination of specimen and comparison sample) has been used in the case of RE alloys. However, many modifications have been necessary due to the high reactivity of the RE alloys and the small amount of sample material usually available. Figure 5 shows the arrangement of the sample and the two comparison samples. By this arrangement the temperature gradients are minimized.

The heat capacity of the crucibles and samples is very small so that small changes of the energy (0.1 cal/sec) yield quite distinct measuring effects. Therefore, the type of reaction occurring can also be determined by the DTA curves. For instance, the enthalpies of melting and of dissolving yield separate peaks. By a quantitative establishment of the heats, a quantitative determination of the amount of phases present in the alloy, e.g., of peritectic reacting phases, is also possible (Reference 29).

Since nearly all intermetallic phases in the Re-Mn systems react peritectically, this possibility has been of great value in determining the phase diagrams. In the case of Gd_6Mn_{23} , this formula could also be determined by DTA. This conclusion is based on measurements which showed that the true composition of Gd_6Mn_{23} must be in the range between $Gd_6Mn_{22.2}$ and $Gd_6Mn_{23.4}$. Figure 6 shows the results of these measurements. The concentration determination has an error of ± 1 wt. percent, due to the accuracy of the X-ray fluorescence analysis.

The practical performance of the measurements is as follows: The samples (0.7 to 1.5 g) were investigated in specially shaped tantalum crucibles. The tantalum crucibles were heated for 5 minutes in open air up to 400° to 500°C. The layer of this tantalum oxide protects

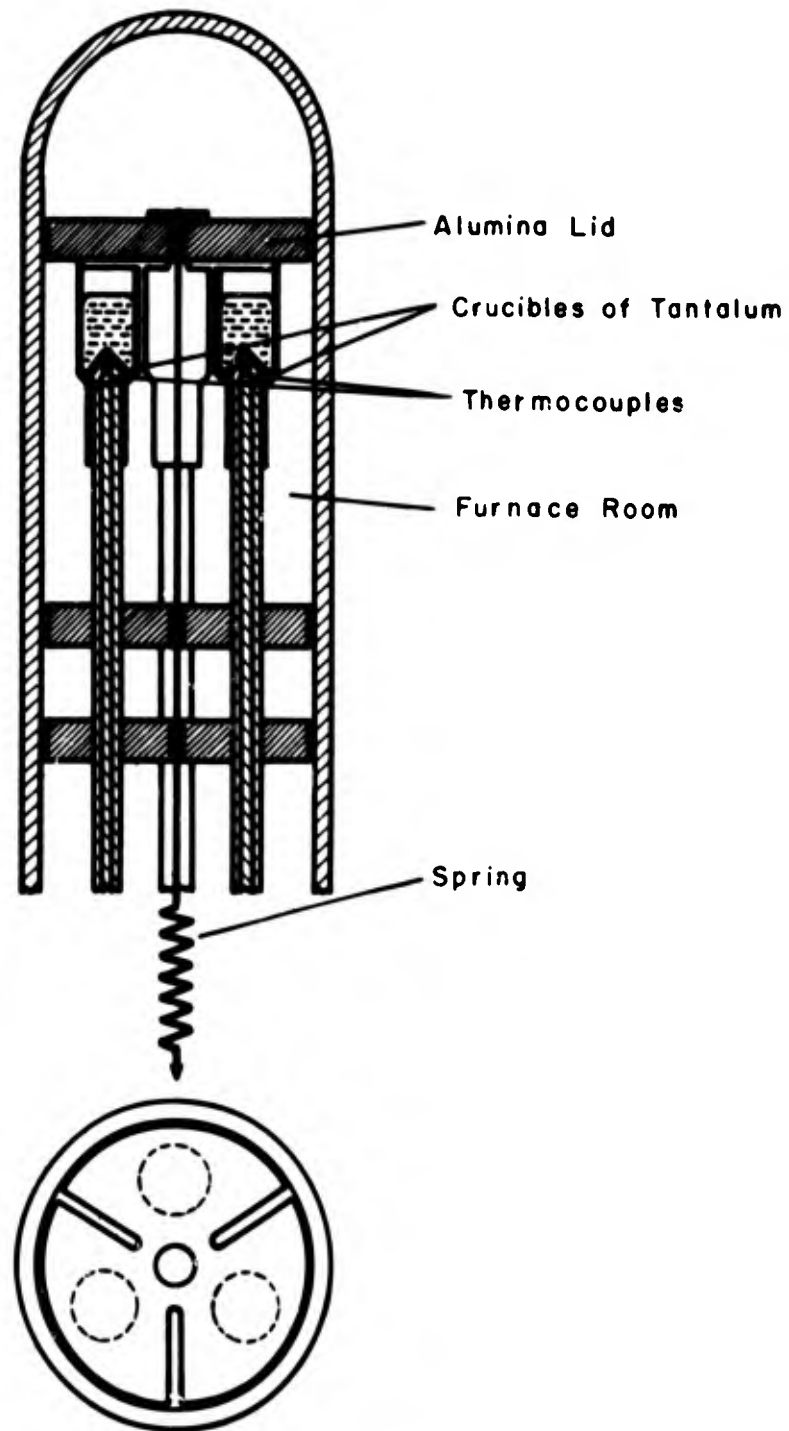


Figure 5. Arrangement for DTA Investigations

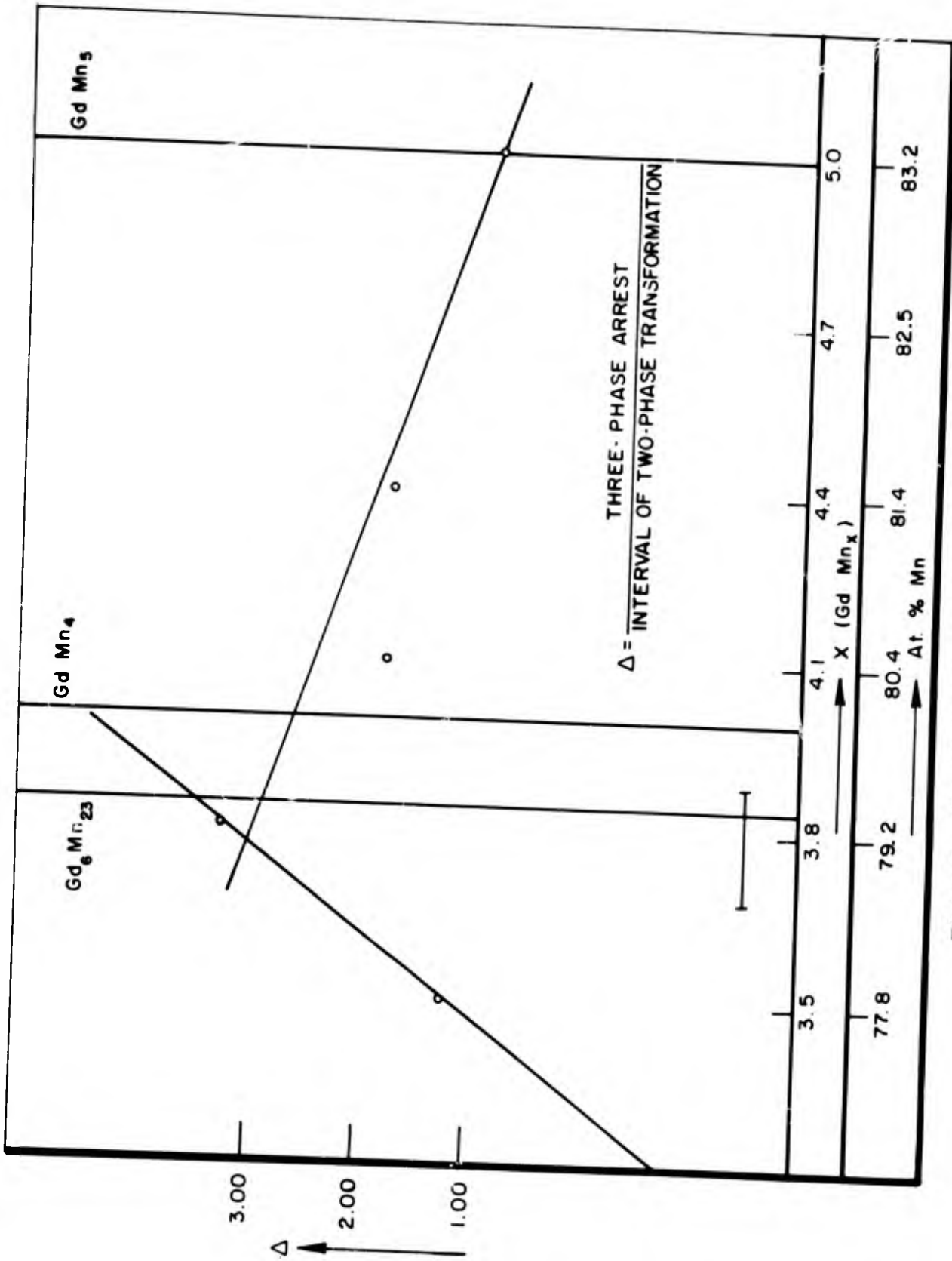


Figure 6. Quantitative Phase Determination by DTA

the tantalum metal against a reaction with the melt up to approximately 1400°C. Therefore an influence of dissolved Ta in the melt can be excluded. Although the thermocouple is separated by 0.7 mm tantalum from the melt, the difference in temperature between the melt and the thermocouple is not more than ±2°C, if the heating rate of the sample is not higher than 10°/min.

An oxidation of the material during the measurements is excluded by the use of very carefully purified (Reference 30) argon as protective gas.

The thermocouples consisted of Pt-Pt/10 percent Rh. They have been kept in small tubes of pure alumina. The emf of these thermocouples has been calibrated with the melting points of pure metals (Al, Ag, and Cu). The longest time of performance for one thermocouple was 15 hours. In this time a variation of the emf, corresponding to a maximum of 2 to 3°C, can be expected.

Since the alloys investigated react peritectically, only the heat evolved during the heating process and not during the cooling process can be used for determining the equilibrium diagram and the equilibrium concentration lines. The starting materials were, in this case, alloys which were single-phase and had been prepared by the amalgam process.

Table II gives the composition of the alloys used for our investigations in wt. percent.

TABLE II

Composition of Alloys Used for DTA Investigation (in Wt. Percent)

Gd	-	Mn	Dy	-	Mn	Ho	-	Mn	Er	-	Mn
90		10	90		10	90		10	89		11
85		15									
84		16	80		20	80		20	77.5		22.5
74		26							72.5		27.5
70		30	70		30	70		30	69.5		30.5
70		30									
62		38							60		40
59.5		40.5									
59		41				45		55			
37.5		62.5	44		56				37.5		62.5
35		65				28		72			
35		65	27		73	23		77	26		74
13		87	14.7		85.3				9.5		90.5
5		95									

THE Gd-Mn SYSTEM

The compounds existing in the Gd-Mn system (Figure 7), GdMn_2 , $\text{Gd}_6\text{Mn}_{23}$, and GdMn_{12} , all react peritectically. The boundaries of stability and the melting enthalpies are contained in Table III.

The alloys with the composition 0 to 30 wt. percent Mn have been prepared by the high frequency induction technique since an equilibrium can be obtained in these alloys within short tempering times. All other alloys have been prepared by the amalgam process.

The compound GdMn_2 forms an eutectic with Gd at 84 wt. percent Gd and 16 wt. percent Mn. The invariant eutectic temperature is 830°C. In the two-phase region between GdMn_{12} and pure Mn, at 87 and 95 wt. percent Mn, measurements with high amplification have been performed. Two equilibrium temperatures, 1085° and 1125°C, could be observed. The solubility of Gd in Mn is approximately 1 at. percent at 1000°C. The observed temperatures of transformation of Mn are slightly lower than are reported for pure Mn, namely, 1094°C β -Mn \rightarrow γ -Mn and 1135°C γ -Mn \rightarrow ζ -Mn.

THE Dy-Mn SYSTEM

The Dy-Mn system (Figure 8) is very similar to the Gd-Mn system. The intermetallic compounds, DyMn_2 , $\text{Dy}_6\text{Mn}_{23}$, and DyMn_{12} , react peritectically. Interesting is the broad peritectic concentration range of the compound $\text{Dy}_6\text{Mn}_{23}$, which covers 30 to 80 wt. percent Mn. The DyMn_2 phase reacts with Dy, yielding an eutectic at a concentration of 12 wt. percent Mn at 855°C. Table IV gives the invariant temperatures of the Dy-Mn system.

A compound with the composition 45 wt. percent Dy appeared single-phase in the X-ray diffraction pattern. This composition corresponds to the formula $\text{Dy}_6\text{Mn}_{23}$. By DTA investigations of an alloy with 85.3 wt. percent Mn, which contained the phase DyMn_{12} and a small amount of free Mn metal, the temperatures of transformation of the Mn allotropes could be measured. These temperatures are 1120° instead of 1135°C and 1075° instead of 1094°C for the transformation γ -Mn \rightarrow ζ -Mn and β -Mn \rightarrow γ -Mn for Mn, saturated with Dy and pure Mn, respectively.

THE Ho-Mn SYSTEM

In the Ho-Mn system (Figure 9) the HoMn_2 , $\text{Ho}_6\text{Mn}_{23}$, and HoMn_{12} compounds are present. The Ho-Mn system is very similar to the Dy-Mn system. The eutectic composition is 12 wt. percent Ho at 875°C. Table V gives the invariant temperatures of the Ho-Mn system. The reaction temperature of HoMn_{12} coincides in the concentration range between HoMn_{12} and Mn with the β -Mn \rightarrow γ -Mn transformation. The transformation of γ -Mn into ζ -Mn is a peritectic equilibrium at 1125°C as in the Gd-Mn system.

THE Er-Mn SYSTEM

In the Er-Mn system (Figure 10) compounds of the same type, namely, ErMn_2 , $\text{Er}_6\text{Mn}_{23}$, and ErMn_{12} , are present. Although all of these phases show a sort of peritectic reaction, only ErMn_2 and $\text{Er}_6\text{Mn}_{23}$ melt incongruently. ErMn_{12} is the limiting case of a peritectic compound since the solidus and the liquidus temperatures are the same. Therefore, ErMn_{12} melts congruently.

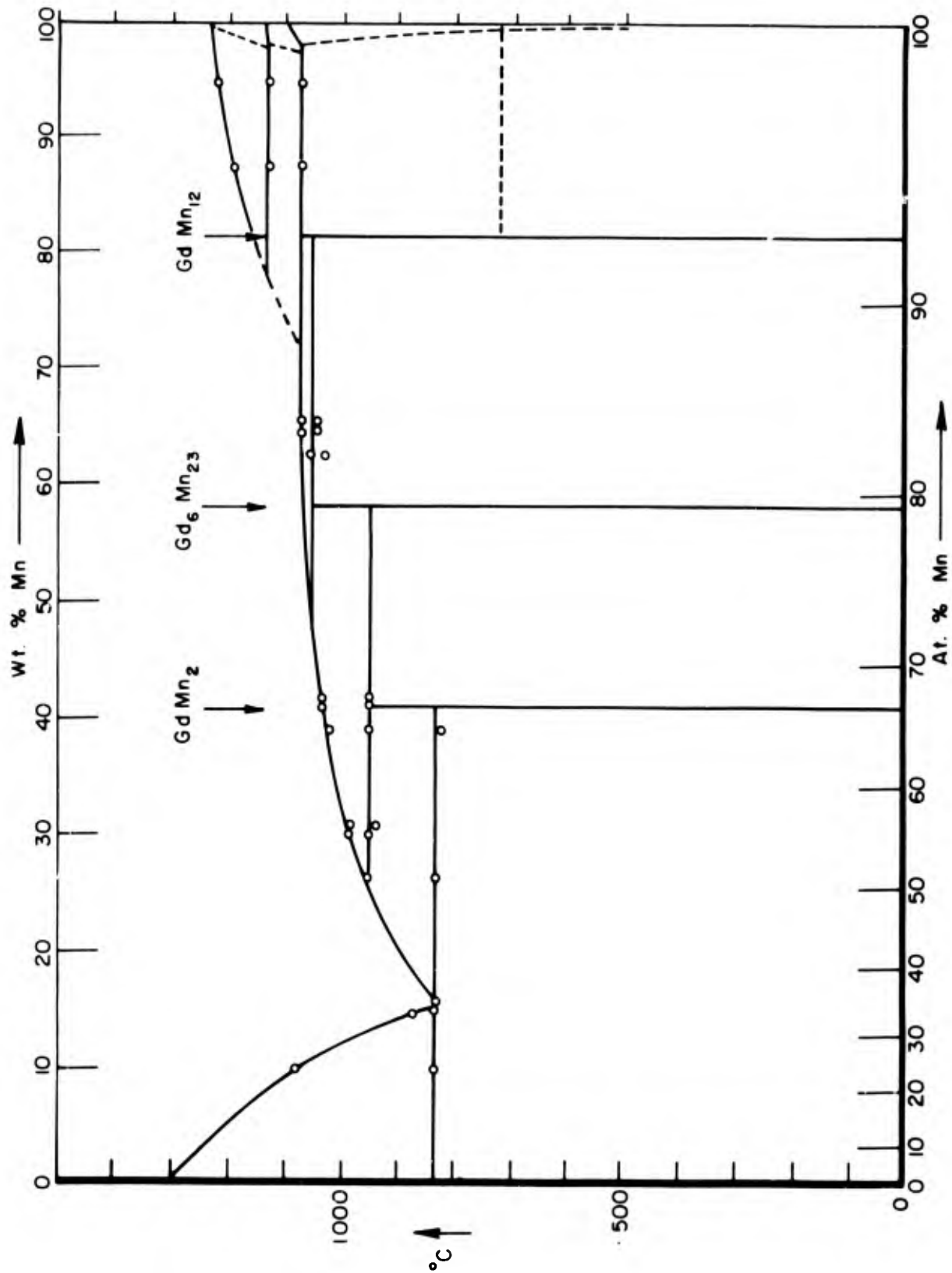


Figure 7. Phase Diagram of the Gd-Mn System

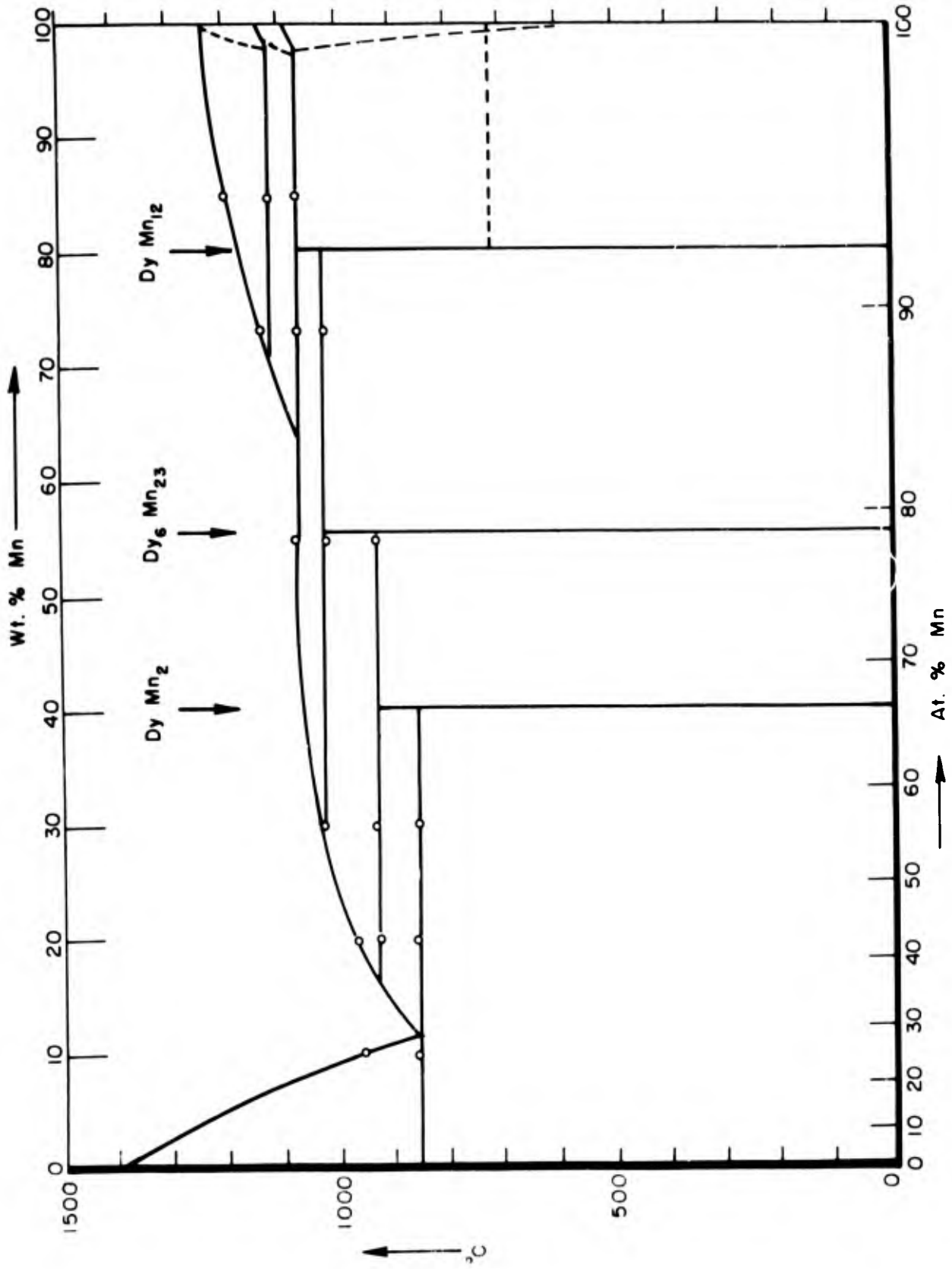


Figure 8. Phase Diagram of the Dy-Mn System

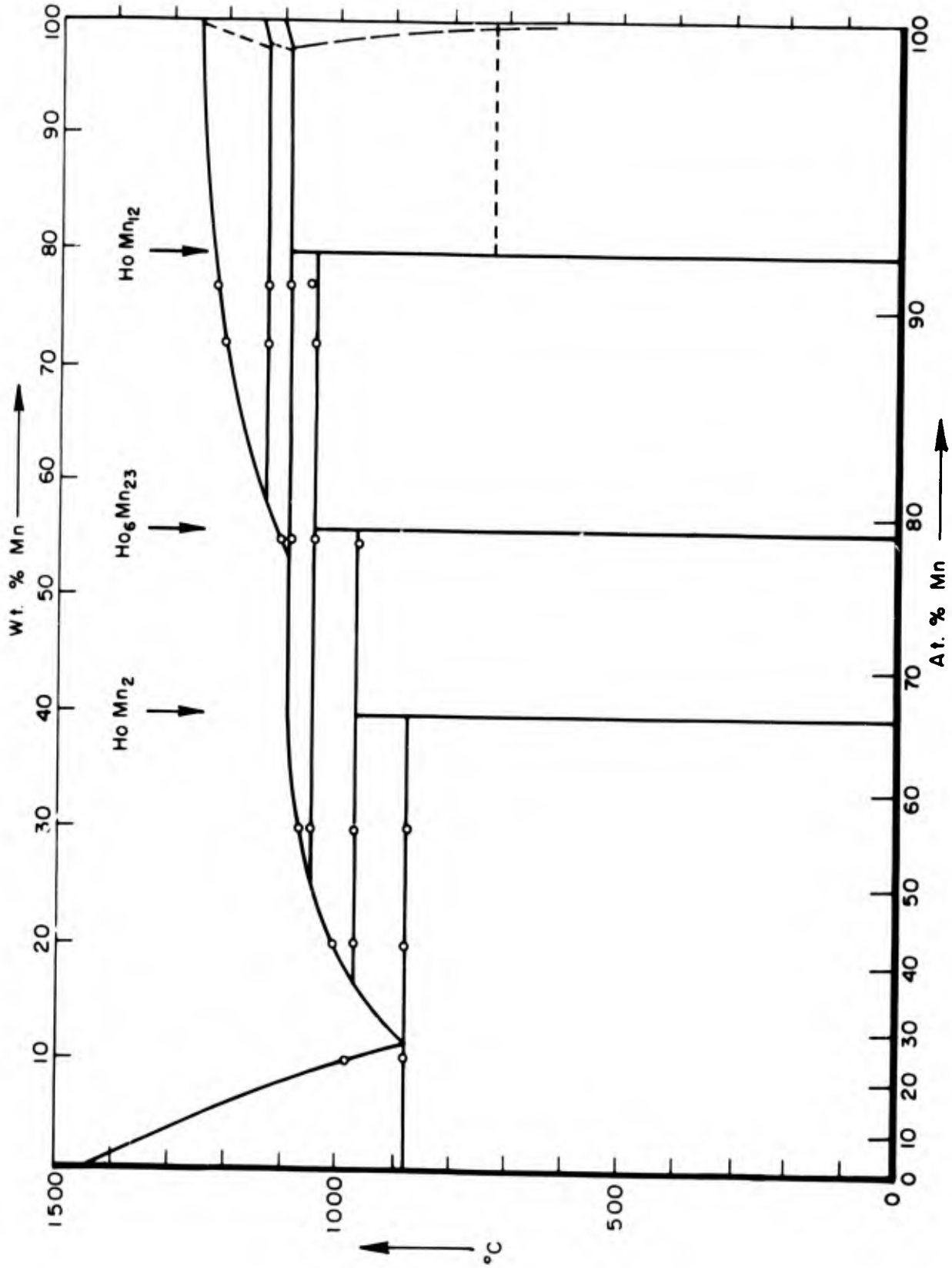


Figure 9. Phase Diagram of the Ho-Mn System

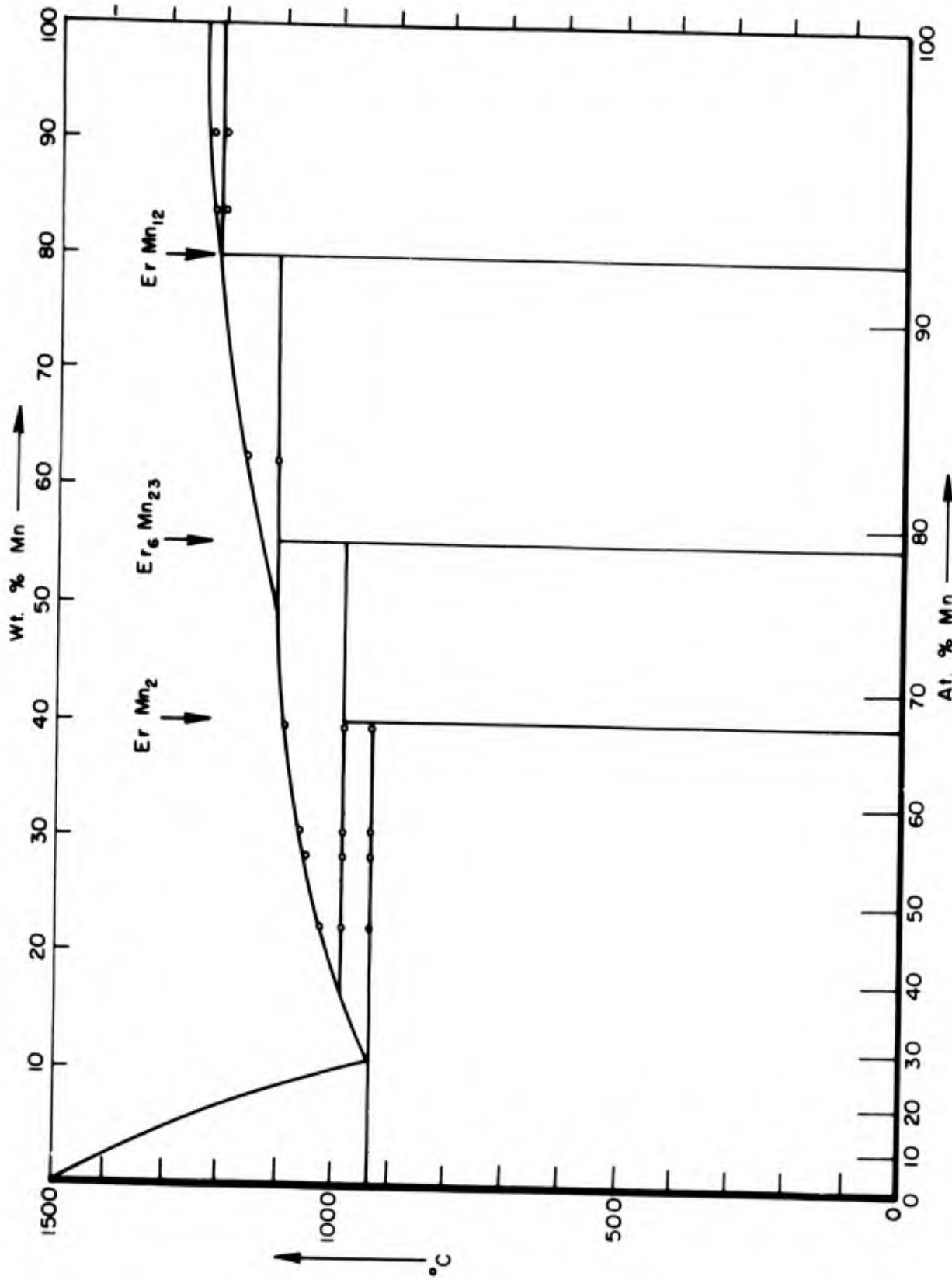


Figure 10. Phase Diagram of the Er-Mn System

TABLE III

Temperatures of Formation and Enthalpies of Gd-Mn Compounds

Reaction	Reaction Temperature	Melting Enthalpy
$\text{Gd}_{\text{sol.}} \rightarrow \text{Gd}_{\text{liqu.}}$	1312°C	2.1 kcal/mol*
$\text{GdMn}_2 \rightarrow \text{Gd}_6\text{Mn}_{23} + \text{melt}$	950°C	1.14 ± 0.1 kcal/mol
$\text{Gd}_6\text{Mn}_{23} \rightarrow \text{GdMn}_{12} + \text{melt}$	1050°C	2.32 ± 0.5 kcal/mol
$\text{GdMn}_{12} \rightarrow \gamma\text{-Mn} + \text{melt}$		

*Reference 23

TABLE IV

Temperatures of Formation of Dy-Mn Compounds

Reaction	Reaction Temperature
$\text{Dy}_{\text{sol.}} \rightarrow \text{Dy}_{\text{liqu.}}$	1407°C
$\text{DyMn}_2 \rightarrow \text{Dy}_6\text{Mn}_{23} + \text{melt}$	930°C
$\text{Dy}_6\text{Mn}_{23} \rightarrow \text{DyMn}_{12} + \text{melt}$	1035°C
$\text{DyMn}_{12} \rightarrow \gamma\text{-Mn} + \text{melt}$	1075°C

TABLE V

Temperatures of Formation of Ho-Mn Compounds

Reaction	Reaction Temperature
$\text{Ho}_{\text{sol.}} \longrightarrow \text{Ho}_{\text{liqu.}}$	1461°C*
$\text{HoMn}_2 \longrightarrow \text{Ho}_6\text{Mn}_{23} + \text{melt}$	965°C
$\text{Ho}_6\text{Mn}_{23} \longrightarrow \text{HoMn}_{12} + \text{melt}$	1045°C
$\text{HoMn}_{12} \longrightarrow \gamma\text{-Mn} + \text{melt}$	1085°C
*Reference 23	

The Er-Mn system can be compared with the Gd-Mn system, as far as the concentration ranges of the peritectics are concerned. The eutectic between Er and ErMn_2 is located at 11.5 wt. percent Mn. This is the smallest amount of Mn present at the eutectic point of all RE-Mn systems. The corresponding temperature is 940°C.

Table VI gives the equilibrium and reaction temperatures.

The compound ErMn_{12} could also be prepared from the melt. Metallographic investigations showed in this case no fringes at the grain boundaries of the crystallites, which would be present in the case of a peritectic reaction. All other compounds prepared by a melting process showed such fringes, which are characteristic of a peritectic reaction.

DISCUSSION

The binary systems of Gd, Dy, Ho, and Er with Mn are very similar. In each of these systems three intermetallic compounds REMn_2 , $\text{RE}_6\text{Mn}_{23}$, and REMn_{12} exist.

These compounds are formed peritectically and have no detectable homogeneity range. The compositions of the intermetallic phases are the same in each system, namely REMn_2 , $\text{RE}_6\text{Mn}_{23}$, and REMn_{12} .

A two-phase region, $\text{RE}\text{Mn}_{12} + \text{melt}$, exists in the Dy-Mn system from approximately 55 to 92.3 at. percent Mn (DyMn_{12}), the corresponding values for the Ho-Mn system are 50 to 92.3 at. percent Mn (HoMn_{12}). In the Gd-Mn and Er-Mn systems the ranges are nearly equal, namely, from 75 to 92.3 at. percent. The concentration range of the two-phase field melt + $\text{RE}_6\text{Mn}_{23}$ is extraordinarily large in the Dy-Mn and Ho-Mn systems, i.e., 37 at. percent Mn \longrightarrow 79.5 at. percent Mn (= $\text{RE}_6\text{Mn}_{23}$). The corresponding ranges in the Gd-Mn and Er-Mn systems, are approximately 50 and 40 at. percent Mn up to the compound $\text{RE}_6\text{Mn}_{23}$. Although the systems have in general similar shape, the ranges of the peritectics are different. The ranges in the Gd-Mn and Er-Mn systems are nearly equal and those of the

TABLE VI

Temperatures of Formation of Er-Mn Compounds

Reaction	Reaction Temperature
$\text{Er}_{\text{sol.}} \longrightarrow \text{Er}_{\text{liqu.}}$	1497°C*
$\text{ErMn}_2 \longrightarrow \text{Er}_6\text{Mn}_{23} + \text{melt}$	990°C
$\text{Er}_6\text{Mn}_{23} \longrightarrow \text{ErMn}_{12} + \text{melt}$	1115°C
$\text{ErMn}_{12} \longrightarrow \gamma\text{-Mn} + \text{melt}$	1210°C
*Reference 23	

Dy-Mn and Ho-Mn are nearly equal to one another. The temperature and the composition corresponding to the eutectic point depend on the melting point of the RE metal. With increasing melting temperatures of the RE metals (Gd: 1312°C, Dy: 1407°C, Ho: 1461°C, Er: 1497°C) the eutectic temperature also increases from 830°C for Gd-Mn to 855°C, 875°C, and 940°C for the Dy, Ho, and Er-Mn systems. The eutectic composition changes in the same series from 84 to 88.5 wt. percent RE metal.

A similar rule cannot be derived for the temperatures of formation for the RE-Mn intermetallic compounds. The temperatures of formation are lowest for DyMn_2 , $\text{Dy}_6\text{Mn}_{23}$, and DyMn_{12} and increase in the order Gd-, Ho-, and Er-Mn. Corresponding to the Y-Mn system investigated by F. Hellawell (Reference 31), peritectic equilibria exist in all RE-Mn systems investigated. These equilibria show a decrease in temperatures of transformation for the Mn metal, which has dissolved some amount of RE metal in the lattice.

SECTION V

MAGNETIC MEASUREMENTS

MEASURING TECHNIQUE

For the measurements on RE compounds a special magnetic balance has been developed (References 18, 19, and 32). This balance takes into account that small samples (10 to 100 mg) of highly reactive RE compounds are to be investigated at low and elevated temperatures in the ferro-, ferri-, or paramagnetic state.

The balance is based on the Faraday principle. The specimens are sealed vacuum tight in thin silica tubes. A 3-kVA magnet with pole pieces of 10-cm diameter allows fields up to 14-kOe to be reached in a 20-mm airgap. This gap allows the mounting of a cooling or heating device, covering the temperature region 80° to 1600°K. Since a force of 0.5 to 1.0 dyne can be measured with an accuracy of 1 percent magnetic moments of at least $5 \cdot 10^{-4}$ emu can be measured with the same accuracy.

MAGNETIC MEASUREMENTS ON RE_6Mn_{23} COMPOUNDS (RE-Gd, -Dy, -Er, -Y)

On specimens of these compounds, prepared by the amalgam process and checked by X-ray diffraction and X-ray fluorescence analysis (Reference 28) for purity and composition, the following measurements have been performed:

Determination of the

- a) Curie temperature,
- b) saturation magnetization at constant temperature,
- c) magnetization and susceptibility as a function of temperature.

The Curie temperature T_c has been determined by measuring the magnetization at 10 to 11.6 kOe as a function of temperature. If σ^2 is plotted versus temperature, a nearly linear curve is obtained in the temperature region below T_c (Reference 33). T_c was obtained by extrapolating this curve to $\sigma^2 = 0$. The Curie temperatures thus obtained are contained in Table VII.

The saturation magnetization at constant temperature has been measured at 80° and 288°K. Lower temperatures were not available. The saturation magnetization at a given temperature was obtained by plotting the magnetization versus $1/H$ and by extrapolating linearly to $H = \infty$. The saturation magnetization at 0°K, $\sigma(H = \infty, T = 0^\circ K)$ yields the μ value, the number of Bohr magnetons contributing to the total magnetization. Only in the case of Y_6Mn_{23} was the temperature dependence of the magnetization between 80° and 300°K smooth enough to allow the extrapolation to a $\sigma(\infty, 0)$ value from the $\sigma(H, T)$ values for $T = 80^\circ$ to $300^\circ K$. All other substances have a temperature dependence of σ , which does not allow such an extrapolation. The measurements of the saturation magnetization at room temperature $\sigma(\infty, 288)$ make it possible to calculate the amount of nonferromagnetic impurities ($RE Mn_2$, $RE Mn_{12}$) in the ferromagnetic RE_6Mn_{23} sample. On the other hand, if series of samples are compared, the sample with the greatest $\sigma(\infty, 288)$ value is likely to be closest to the stoichiometric

TABLE VII

Magnetic Data of RE_6Mn_{23} , $RE Mn_{12}$, and $RE Mn_2$ Compounds

	θ °K	T_c °K	μ_{eff} Compound Meas.	μ_{eff} RE^{3+} Calculated*	$\mu = g J$ Compound Measured*	$\mu = g J$ RE^{3+} Calculated
Sm_6Mn_{23}	85	439	5.04	1.53	0.5	0.7
Gd_6Mn_{23}	- 90	468	10.04	7.94	8.4	7.0
Dy_6Mn_{23}	25	443	11.47	10.6	8.3	10.0
Ho_6Mn_{23}	- 5	434	11.83	10.6	8.2	10.0
Er_6Mn_{23}	30	415	10.56	9.6	7.6	9.0
Y_6Mn_{23}	475	486	2.35	0.0	2.06	0.0
$GdMn_{12}$	- 25	-	17.2	7.94		
$DyMn_{12}$	-398	110(T_n)	16.3	10.6		
$ErMn_{12}$	- 65	-	13.2	9.6		
$GdMn_2$	45	(86)(T_n)	8.86	7.94	-	-
$DyMn_2$	- 15	-	10.9	10.6	-	-
$ErMn_2$	- 90	-	10.1	9.6	7.72***	9.0

*Reference 37
**Reference 38
***Reference 36

composition of the phase. By such measurements on Gd_6Mn_{23} samples the formula RE_6Mn_{23} was confirmed.

The measurements of magnetization and susceptibility as a function of temperature have been performed at 10 to 10.3 kOe in the temperature range from 80° to approximately 1200°K. The results, obtained on Gd_6Mn_{23} , Dy_6Mn_{23} , Er_6Mn_{23} , and Y_6Mn_{23} are shown in the Figures 11, 12, 13, and 14.

The temperature dependence of the magnetization σ ($\text{emu/g} = \text{Gauss cm}^3 \text{g}^{-1}$) of Gd_6Mn_{23} is regular from T_c down to approximately 200°K. Near this temperature, however, a point of inflection is observed and the magnetization rises very sharply at lower temperatures. A second point of inflection must be present below 80°K, since σ must reach 0°K with the slope zero. The plot of the reciprocal susceptibility $1/\chi_g$ versus temperature is linear from approximately 850° to 1000°K. By extrapolating this line the paramagnetic Curie-temperature θ is obtained. This straight line corresponds to a Curie-Weiss law $1/\chi_g = (R - \theta)/C_g$.

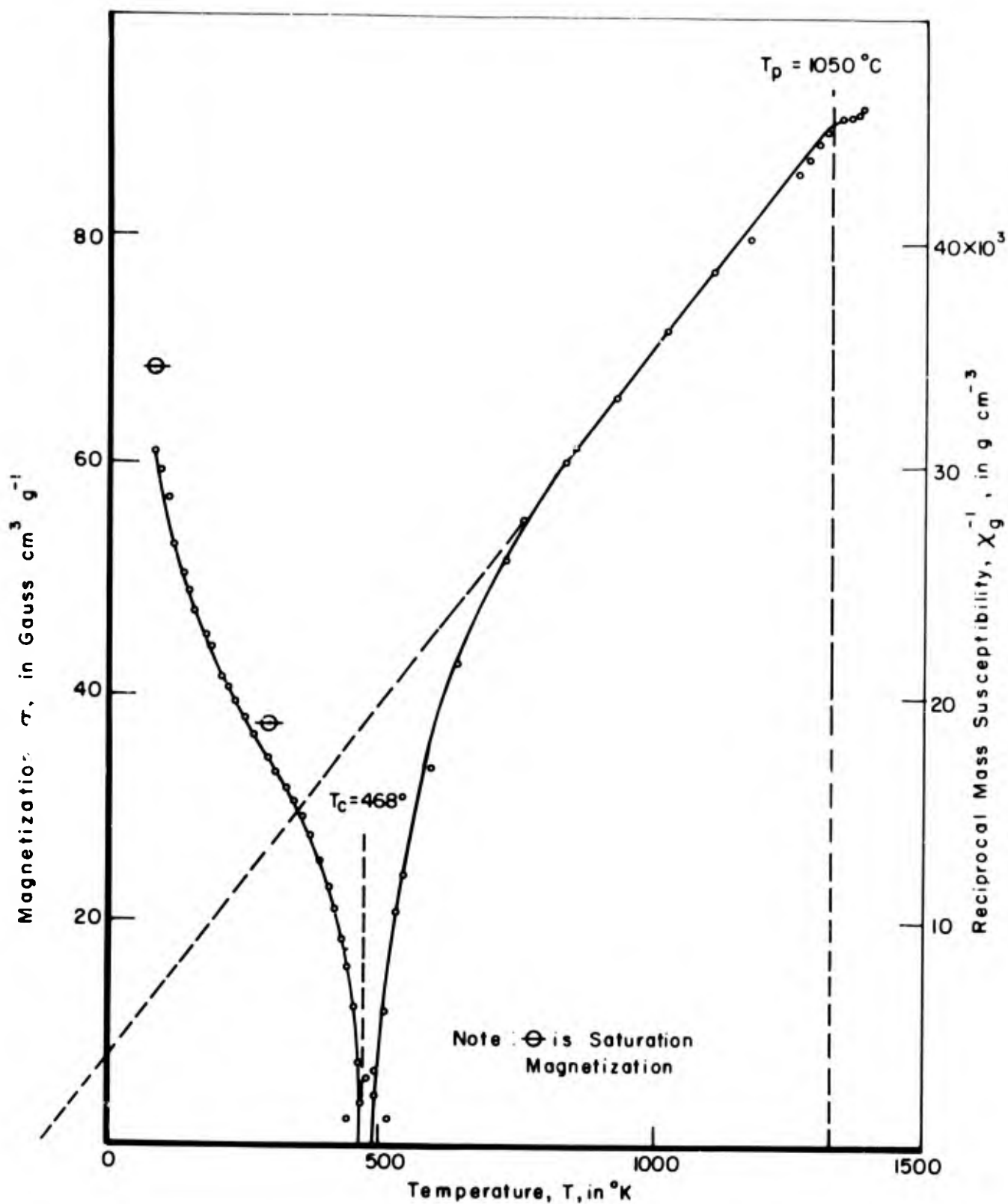


Figure 11. Magnetization σ and Reciprocal Mass Susceptibility $1/\chi_g$ of Gd_6Mn_{23} Versus Temperature

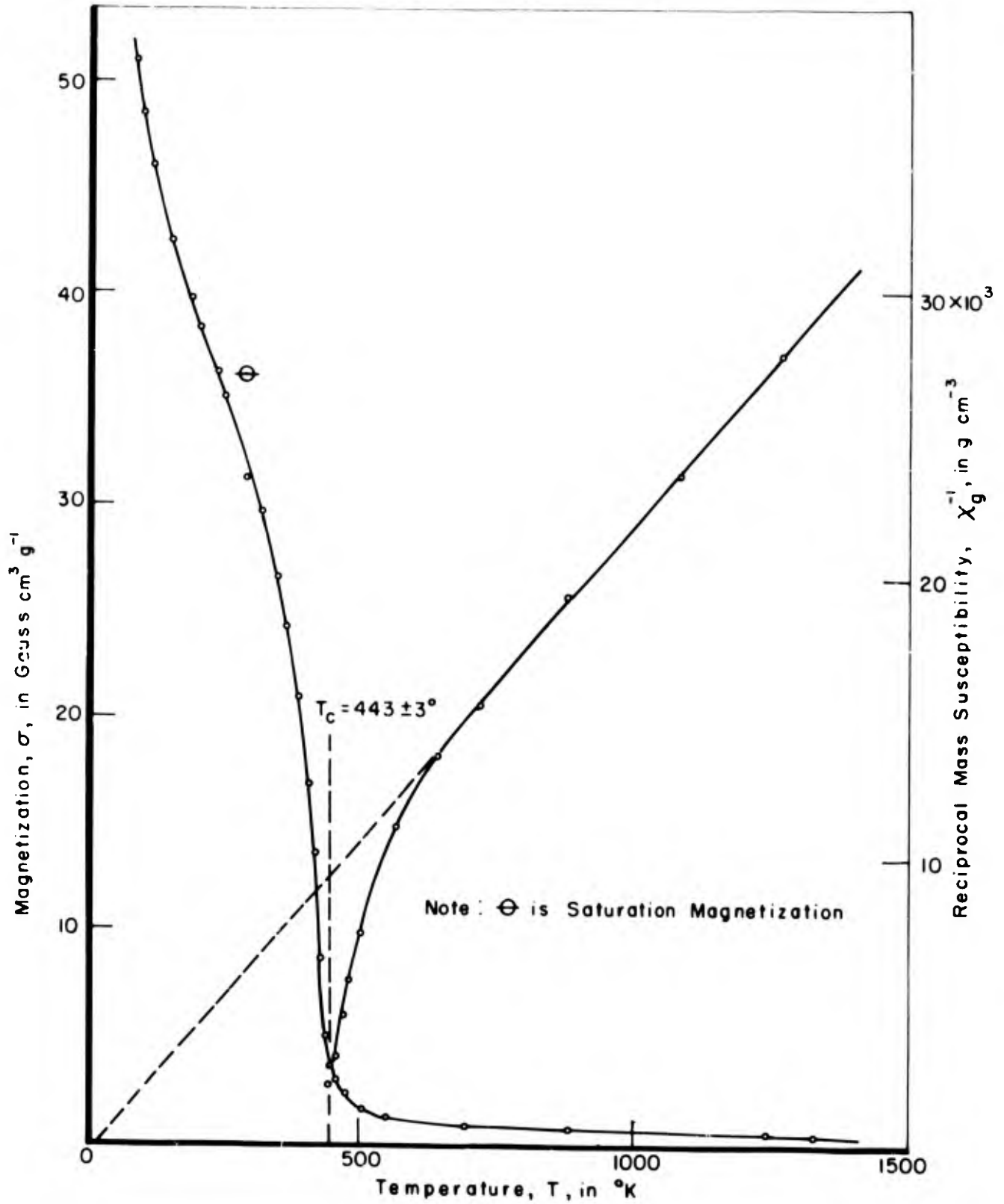


Figure 12. Magnetization and Susceptibility of $\text{Dy}_6\text{Mn}_{23}$ Versus Temperature

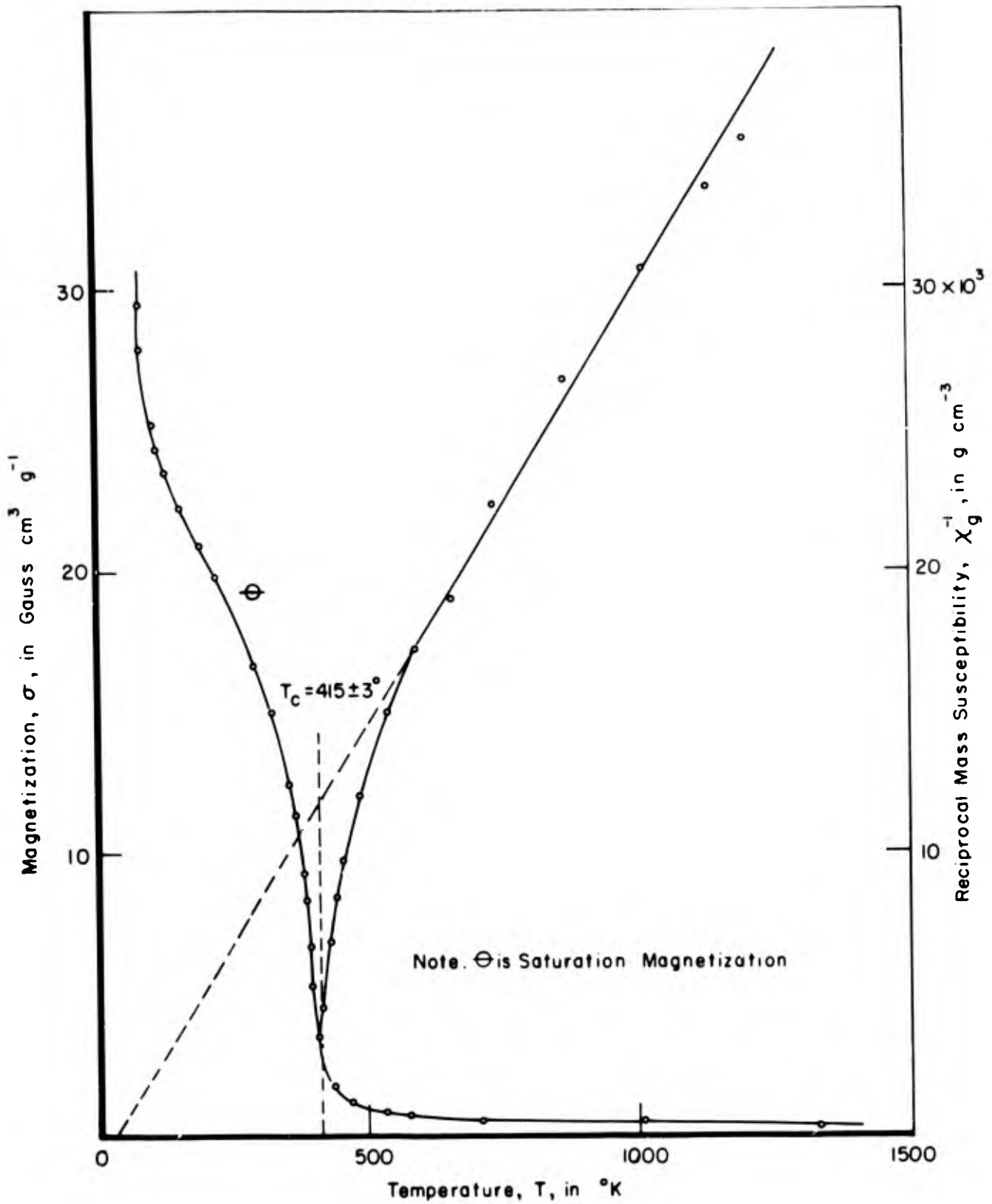


Figure 13. Magnetization and Susceptibility of $\text{Er}_6\text{Mn}_{23}$ Versus Temperature

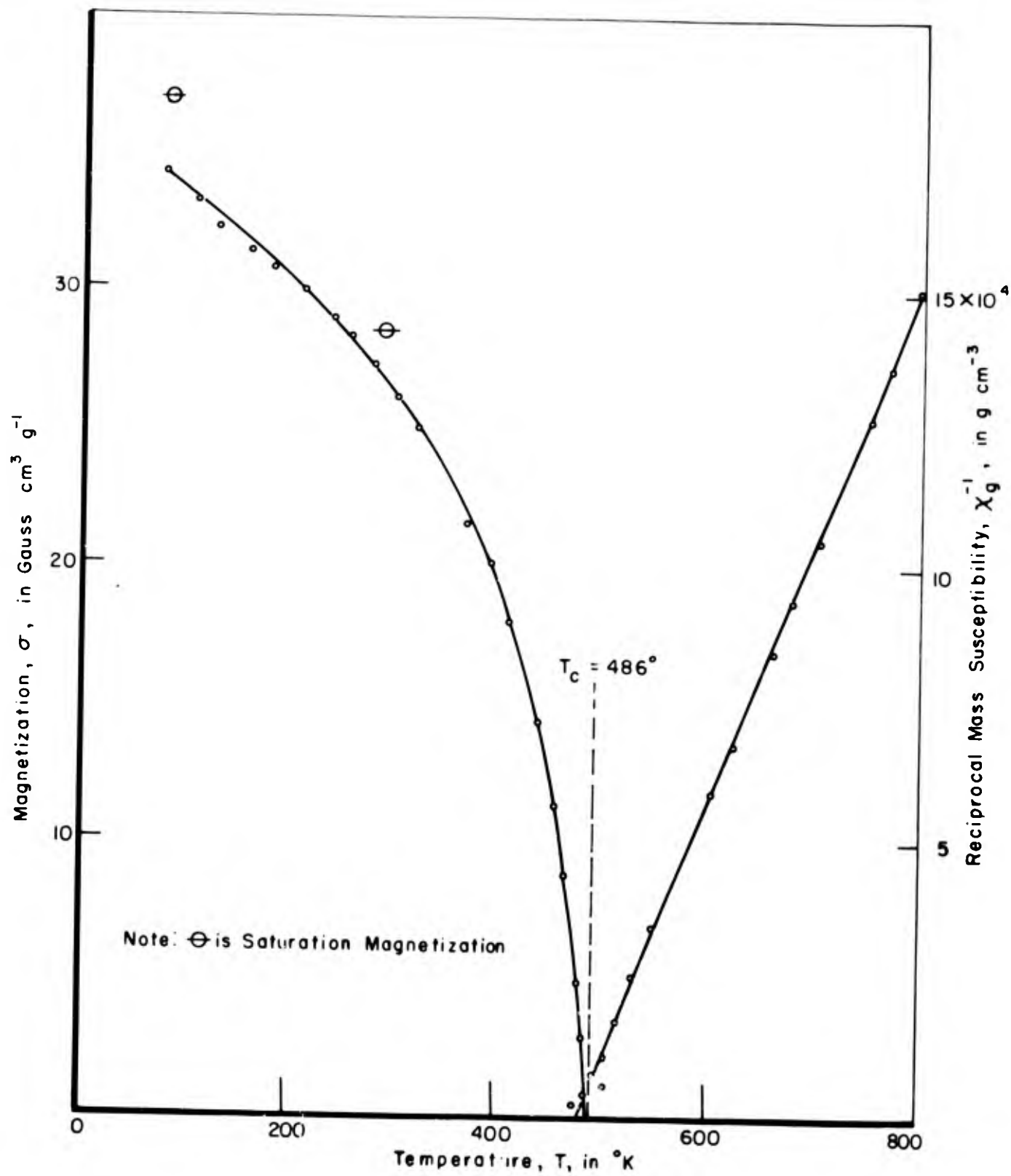


Figure 14. Magnetization and Susceptibility of Y_6Mn_{23} Versus Temperature

From the slope of this curve the effective Bohr-magneton number μ_{eff} is calculated according to: $\mu_{\text{eff}} = 2.83 \sqrt{C_g M}$ (M . . . molal weight). Below 850°K down to T_c a deviation of $1/\chi_g$ from a straight line is observed. The plot of $1/\chi_g$ versus temperature yields a hyperbola with the asymptotes $1/\chi_g = T/C + 1/\chi_0$ and $T = T_c$. The fact that T_c and θ are different by more than 500°K, that $1/\chi_g$ shows a hyperbolic temperature dependence, and, finally, that μ_{eff} and μ , calculated from $\sigma(\infty, 0)$, are markedly different, can be explained according to Neel (Reference 34) by a ferrimagnetic coupling of the magnetic moments below T_c . The data concerning $\text{Gd}_6\text{Mn}_{23}$ are based on repeated measurements, performed on a selected specimen of the composition $\text{Gd}_6\text{Mn}_{23}$ (79.3 at. percent Mn). Other specimens with 76.2 and 83.3 at. percent Mn yielded similar results, although the saturation magnetization was naturally lower because of the presence of GdMn_2 or GdMn_{12} in the samples. By these measurements the results of earlier investigations (References 4 and 18) are confirmed.

The compounds $\text{Dy}_6\text{Mn}_{23}$ and $\text{Er}_6\text{Mn}_{23}$ have a behavior similar to $\text{Gd}_6\text{Mn}_{23}$. The magnetization also shows a point of inflection at approximately 200°K. In the temperature region from 700° to 1400°K $1/\chi_g$ depends linearly on the temperature. From 700°K to T_c the $1/\chi_g$ plot deviates from a straight line. The same considerations which lead to the conclusion that $\text{Gd}_6\text{Mn}_{23}$ is ferrimagnetic can be applied also to $\text{Dy}_6\text{Mn}_{23}$ and $\text{Er}_6\text{Mn}_{23}$.

The magnetic data of $\text{Sm}_6\text{Mn}_{23}$ and $\text{Ho}_6\text{Mn}_{23}$, contained in Table VII, are based on measurements given earlier (Reference 18) but have been re-calculated according to the formula $\text{RE}_6\text{Mn}_{23}$. In general, $\text{Sm}_6\text{Mn}_{23}$ and $\text{Ho}_6\text{Mn}_{23}$ also show the same temperature dependence of magnetization and susceptibility as the other $\text{RE}_6\text{Mn}_{23}$ compounds and must therefore also be regarded as ferrimagnetic.

Magnetic measurements on Y_6Mn_{23} facilitate the interpretation of the magnetic behavior of other $\text{RE}_6\text{Mn}_{23}$ compounds since Y, in contrast to the majority of the RE metals, has no magnetic moment. From Figure 14 it can be seen that the σ versus T curve shows no point of inflection. The extrapolation of σ to $T = 0$ is possible with reasonable accuracy. The $1/\chi_g$ versus T plot is a straight line from T_c ($T_c = 486^\circ\text{K}$) up to at least 800°K. Therefore, T_c and θ are nearly equal. From these facts and from the calculated μ_{eff} value it must be concluded that Y_6Mn_{23} is ferromagnetic.

MAGNETIC MEASUREMENTS ON REMn_{12} COMPOUNDS (RE-Gd, -Dy, -Er)

Figure 15 contains the results of measurements on GdMn_{12} , DyMn_{12} , and ErMn_{12} . Magnetic measurements on REMn_{12} compounds, which are paramagnetic or antiferromagnetic, are made difficult by the fact that the peritectically formed REMn_{12} compounds nearly always contain traces of the strongly magnetic $\text{RE}_6\text{Mn}_{23}$ compounds. Since the amalgam process yielded REMn_{12} specimens with only a small content of $\text{RE}_6\text{Mn}_{23}$ (below 3 percent), the data given in Figure 15 can be regarded as reliable. The reciprocal susceptibility plot of DyMn_{12} is linear from 800° down to 110°K. At this temperature a minimum is observed.

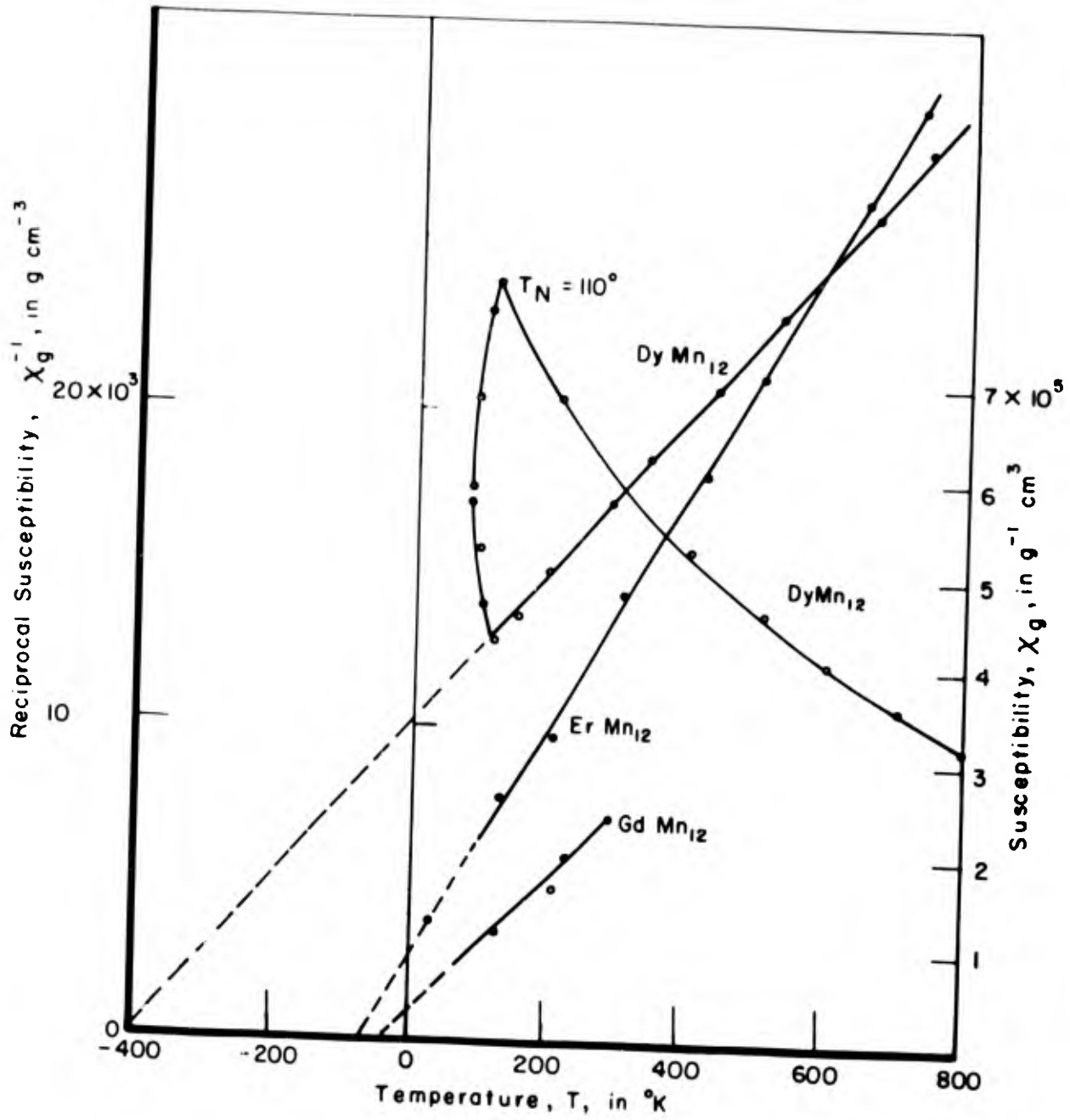


Figure 15. Reciprocal Susceptibility $1/\chi_g$ of $GdMn_{12}$, $DyMn_{12}$, and $ErMn_{12}$ Versus Temperature, and Susceptibility of $DyMn_{12}$ Versus Temperature

The paramagnetic Curie temperature obtained by extrapolating the linear part of the $1/\chi_g$ plot is -398°K . This fact together with the maximum value of χ_g at 110°K suggests that DyMn_{12} is antiferromagnetic below the Neel temperature T_n of 110°K .

GdMn_{12} and ErMn_{12} also show a linear $1/\chi_g$ plot from 700° down to 80°K and a negative θ value. A maximum of χ_g , however, could not be observed. Nevertheless, an antiferromagnetic coupling of the moments below 80°K is very likely.

MAGNETIC MEASUREMENTS ON REMn_2 COMPOUNDS (RE-Gd, -Dy, -Er)

The magnetic properties of some REMn_2 compounds have been determined earlier (References 35 and 36) at low temperatures (2.1° to 150°K). Figure 16 contains additional measurements obtained in the temperature region from 80° to approximately 1200°K . These compounds are also likely to contain traces of $\text{RE}_6\text{Mn}_{23}$ compounds. A correction was applied when such traces were detected.

The $1/\chi_g$ plot of GdMn_2 is linear from approximately 1000° down to 100°K . At 86°K , however, there seems to be a maximum in the χ_g curve, indicating a Neel point. The measurements performed on DyMn_2 are to be regarded as preliminary, since the sample investigated contained 7.5 percent $\text{Dy}_6\text{Mn}_{23}$, an influence which cannot be corrected completely. Nevertheless, the calculated μ_{eff} value seems reasonable. θ is negative; therefore, the fact of antiferromagnetic ordering at low fields (Reference 35) and perhaps ferromagnetic ordering at high fields is supported. The temperature dependence of $1/\chi_g$ of ErMn_2 is a straight line from 1200° down to approximately 400°K , where a slight deviation, due to an $\text{Er}_6\text{Mn}_{23}$ contamination, is observed. The negative value of θ indicates ferro- or antiferromagnetic coupling of the moments at lower temperatures. This corresponds to the ferromagnetic coupling of the RE moments and antiparallel coupling of small Mn moments, observed by neutron diffraction measurements below the transition point of 25°K (Reference 36).

The μ and μ_{eff} values in Table VII refer to one RE atom, i.e., the calculations are based on the formulas $\text{RE}\text{Mn}_{3.83}$, REMn_{12} , and REMn_2 .

DISCUSSION

A detailed and fundamental interpretation of the above given measurements is made rather complicated by the following facts:

In the RE-Mn compounds both the RE atoms and the Mn atoms bear a magnetic moment. Therefore, not only the same problems arise which are encountered when the magnetic

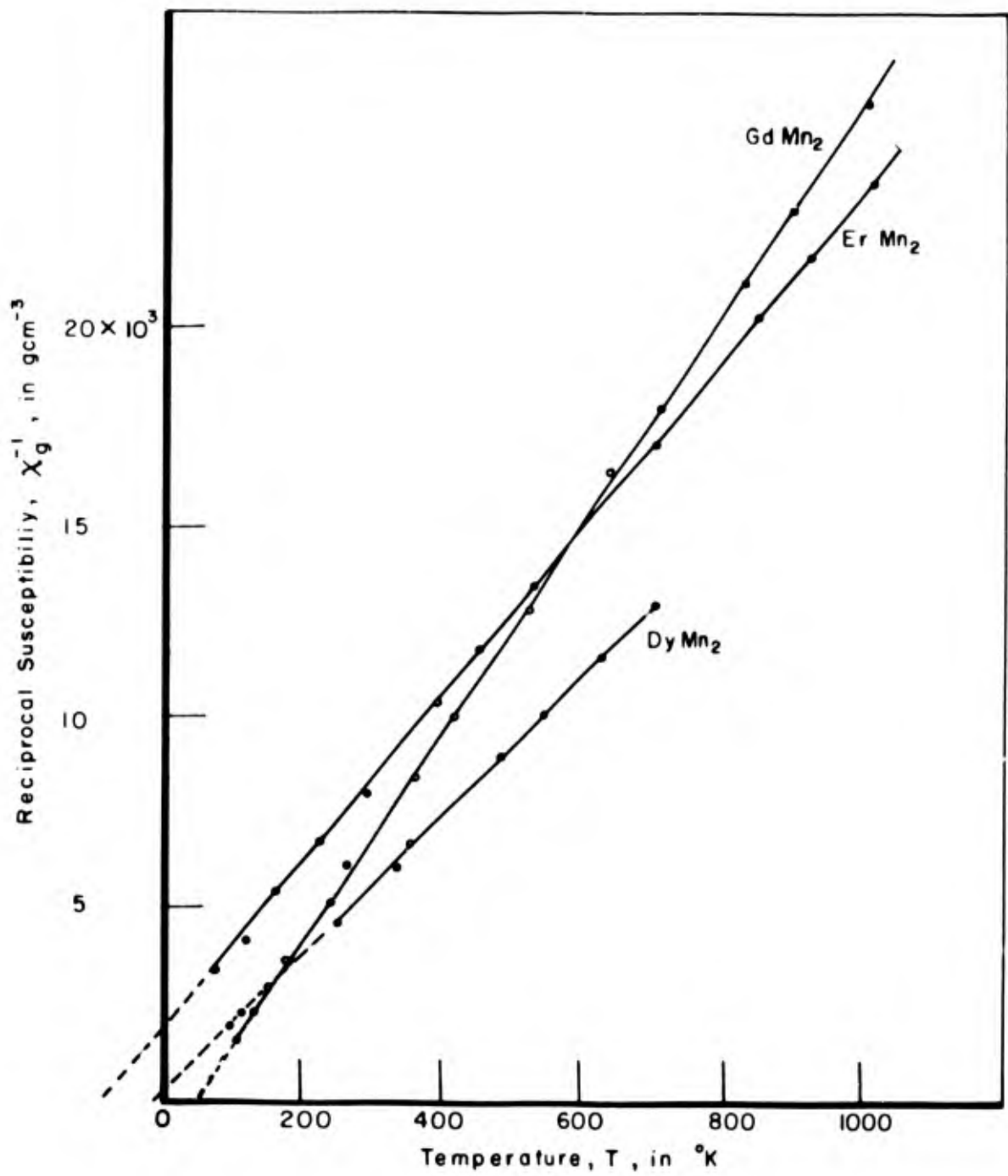


Figure 16. Reciprocal Susceptibility $1/\chi_g$ of GdMn_2 , DyMn_2 , and ErMn_2 Versus Temperature

properties of RE metals or 3-d metals are discussed, but also problems because of the interaction between RE and Mn sublattices. Such an interaction can change not only the direction, but also the value of the moments attributed to each atom. For example, the moment of Mn can not even be regarded as always the same in analogous compounds. Furthermore, the moments may be changed by electron transfer and by crystal field effects.

On the other hand, our knowledge of the magnetic and structural properties of RE-Mn compounds has now reached a point which not only allows but seems to necessitate at least a cautious interpretation.

Y_6Mn_{23} may be used as a starting point. Since Y bears no detectable moment, only the Mn atoms contribute to the μ or μ_{eff} value. These values are nearly the same and Y_6Mn_{23} must be regarded as purely ferromagnetic, i.e., all Mn moments couple parallel. Mn bears a moment of approximately 0.5 to 0.6 μ_B in this compound. This value agrees well with neutron diffraction measurements on α -Mn (Reference 39). The same moment seems to apply in general also to other RE-Mn compounds; however, a decrease of the magnetic moment of each Mn atom with increasing RE moment is observed. Neutron diffraction measurements on $ErMn_2$ (Reference 36), which suggested an Mn moment near zero, can be differently interpreted with a moment of up to 0.3 μ_B for Mn and canted spins.

The μ_{eff} values of the other RE_6Mn_{23} compounds agree well with the concept that there are RE^{3+} ions present and Mn has a moment between 0.2 and 0.6 μ_B .

The temperature dependence of $1/\chi_g$ seems to necessitate some sort of ferrimagnetic coupling in these compounds (References 4 and 18). This conclusion is supported by a comparison between the μ and μ_{eff} values with the RE moments. For example, the measured μ -values of Dy_6Mn_{23} and Er_6Mn_{23} can only be obtained (if an alteration of the RE moments at low temperatures by crystal field quenching is excluded) if the majority of the Mn moments couple antiparallel.

Gd_6Mn_{23} , however, has a μ value which is higher than the μ value of the Gd^{3+} ion and seems to be ferromagnetic at low temperatures and high fields (Reference 38). This conclusion, on the other hand, seems inconsistent with the temperature dependence of $1/\chi_g$, which does not follow Curie-Weiss behavior.

The temperature dependence of the magnetization of the RE_6Mn_{23} compounds (see References 4, 18, 21, and 38 and Figures 11, 12, and 13) can give some hint in answer to this question. The temperature dependence of the magnetization of Gd_6Mn_{23} , Dy_6Mn_{23} , and Er_6Mn_{23} is not a curve with continuously decreasing slope (as, e.g., Y_6Mn_{23}), but has at least one point of inflection near 200°K. Obviously from T_C down to 200°K only a gradual ordering of the moments takes place; but below 200°K complete ordering is achieved. Such a mechanism is made likely by the complex crystal structure of the RE_6Mn_{23} compounds.

The $\text{RE}_6\text{Mn}_{23}$ structure contains 116 atoms in the unit cell. Although the RE positions are crystallographically equivalent, there exist four different Mn positions. It is probable that the moments of the RE atoms and of the different Mn atoms order at different temperatures and at different field strengths in a varied and complex way. The behavior of $\text{Gd}_6\text{Mn}_{23}$, e.g., may be explained by a simple two sublattice model, i.e., that below T_c first all Gd moments couple, yielding a ferromagnetic coupling at 0°K and infinite field. However, the data obtained in the paramagnetic region indicate that such a simple model is not sufficient. Another and perhaps more accurate model is based on several independent Mn sublattices, corresponding to the different Mn positions. In this case it is possible to assume that some or all Mn moments couple first ferrimagnetically to the Gd moments and only in higher fields, and at very low temperatures all different Mn moments are aligned parallel to the Gd moments. In this or a similar case all $\text{RE}_6\text{Mn}_{23}$ compounds must be regarded as ferrimagnetic at temperatures immediately below T_c and at low fields. Then with decreasing temperature, depending also on the field strength, various modes of ferrimagnetic or even antiferromagnetic structures are passed. Ultimately, at high field strengths, proceeding from the different ferrimagnetic states, complete parallel coupling of all moments in the case of $\text{Gd}_6\text{Mn}_{23}$ and complete antiparallel coupling of all Mn moments with the RE moments in the other $\text{RE}_6\text{Mn}_{23}$ compounds is achieved.

Although this proposed mechanism can explain the experimental results and is consistent with theoretical considerations, the exact determination of the complex magnetic state of $\text{RE}_6\text{Mn}_{23}$ compounds can only be achieved by neutron diffraction experiments, which are especially difficult in the case of $\text{Gd}_6\text{Mn}_{23}$.

A similar mechanism may be operative on the behavior of the REMn_{12} compounds. Although these compounds seem to be antiferromagnetic below approximately 100°K, at lower temperatures and higher fields a different ordering is possible, especially because in the structure of the REMn_{12} compounds three crystallographically different Mn atom positions are present. The μ_{eff} values are consistent with the moments of RE^{3+} ions and a moment between approximately 0.2 and 0.5 μ_B for each Mn atom.

Finally, the REMn_2 compounds also occur in different magnetic states, antiferromagnetic at low fields and ferrimagnetic at high fields (Reference 35). Since these compounds can occur either in a hexagonal or in a cubic structure, there are also different modes of coupling of the moments possible. In these compounds Mn has apparently a moment of 0.2 to 0.5 μ_B , while the RE atom is trivalent.

In general, the magnetic behavior of RE-Mn compounds can be understood as a mutual interaction of different ferrimagnetic states. The details of these transitions, however, need further investigations, especially at low temperature and by neutron diffraction techniques.

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<i>(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)</i>		
1 ORIGINATING ACTIVITY (Corporate author) Institute of Technology (Technische Hochschule Wien) Vienna, Austria		2a REPORT SECURITY CLASSIFICATION Unclassified
		2b GROUP
3 REPORT TITLE RARE EARTH - MANGANESE ALLOYS, THEIR PREPARATION, CRYSTAL STRUCTURES, PHASE DIAGRAMS, AND MAGNETIC PROPERTIES		
4 DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Report 1 April 1962 - 30 March 1965		
5 AUTHOR(S) (Last name, first name, initial) Lihl, Franz and Kirchmayr, Hans R.		
6 REPORT DATE January 1967	7a TOTAL NO OF PAGES 46	7b NO OF REFS 39
8a CONTRACT OR GRANT NO 61(052)-609	9a ORIGINATOR'S REPORT NUMBER(S) AFML-TR-66-366	
b. PROJECT NO	9b OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c		
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10 AVAILABILITY/LIMITATION NOTICES Distribution of this document is unlimited. In DDC. Available from CFSTI.		
11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY Air Force Material Laboratory Wright-Patterson AFB, Ohio 45433	
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