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The magnetic properties of high purity scandium, yttrium,
lanthanum and lutetium and the effects of impurities on
these properties

by

John Joseph Croat

A Dissertation Submitted to the
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I. INTRODUCTION

The group of elements commonly known as the rare earths include the lanthanide series and the elements scandium, yttrium and lanthanum. Scandium, yttrium and lanthanum are all reported to have a noble gas plus a $(n-1)d\ ns^2$ electronic configuration. For elements following scandium and yttrium in the periodic table the electrons are added to the $(n-1)d$ orbitals. However the elements following lanthanum are formed by the addition of electrons to the 4f orbitals which become more stable than the 5d orbitals. This continues across the periodic table until all seven of the 4f orbitals are occupied. Thus there are 14 lanthanides plus scandium, yttrium and lanthanum for a total of 17 rare earths.

The study of the magnetic properties of the rare earth metals and alloys has commanded a great deal of interest primarily because most of these elements have at least one unpaired 4f electron which gives rise to large magnetic moments. The rare earths scandium, yttrium, lanthanum and lutetium, however, have no unpaired 4f electrons but are still of great interest because the smaller contributions to the susceptibility are not swamped by the temperature dependent paramagnetism and enables a more accurate determination of these contributions. The reason that the magnetic susceptibilities of these metals are not well known is due not to the difficulty of measuring the small moments of approximately 10^{-6}

emu/gram but more importantly to the lack of well characterized and highly pure samples.

Susceptibility results for both single and polycrystalline scandium have been reported by a number of groups. Despite this neither χ or its temperature dependence have been well established. Even the most recent results disagree by as much as 8% at room temperature and considerably more than this at low temperatures. Similar discrepancies are also found in the case of yttrium and lanthanum. These discrepancies are generally thought to result from varying amounts of impurities in the measured specimens. To date, however, little is known of the effect of these impurities on the susceptibility. This is particularly true in the case of gaseous impurities. In the bulk of the previously reported data no analysis of these impurities was given. While analytical results for paramagnetic impurities are more frequently reported, the large effect that even minute quantities of these impurities have at low temperatures requires that these analyses be very accurate in order to estimate their contribution to the susceptibility. Unfortunately, analyses of the required accuracy are difficult to obtain at this time. This is further complicated by the fact that the effective moments and paramagnetic Curie temperatures of these impurities in metallic solutions are not well known. It is clear, therefore, that before reliable results of the magnetic properties of these rare earth metals can be obtained, very high purity samples must be prepared.

In recent years a study was undertaken at the Ames Laboratory to increase the overall purity of the rare earth metals by several orders of magnitude. This effort has resulted in significant increases in purity, especially with regard to gaseous impurities, tantalum and other rare earths. In addition significant progress has been made in the analysis of these metals by the various analytical groups, especially in mass spectroscopy. Through the introduction of calibrated standards the analysis of rare earths can now be determined with an accuracy of $\pm 20\%$ in the 1 ppm range. This contrasts with other laboratories where the amount of rare earth impurities is known to within only 100 to 200% of the amount present.

Due to both the greater purity and increased confidence in the analytical results, a study of the magnetic properties of scandium, yttrium, lanthanum and lutetium was undertaken. The magnetic susceptibilities of these metals were measured from approximately 1.5 to 300°K by the Faraday technique. In the case of scandium, yttrium and lutetium both single and polycrystalline specimens were measured. Attempts to grow single crystals of lanthanum were unsuccessful and hence only polycrystalline dhcp specimens were measured. A systematic study of the effect of nonmagnetic impurities on the susceptibility of these metals, particularly scandium, was carried out. The behavior of dilute magnetic rare earth impurities in a scandium matrix was also studied. In particular the susceptibility of

a series of dilute scandium-gadolinium and scandium-erbium alloys was investigated.

II. HISTORICAL

A. Scandium

The first published results on the susceptibility of polycrystalline scandium was by Bommer¹ in 1939. His room temperature value of 7.0×10^{-6} emu/gram is the highest reported to date but his sample is believed to have had considerable impurities, including 85 wt % KCl which he corrected for. In 1956 Iya² reported a room temperature susceptibility of $.24 \times 10^{-6}$ emu/gram which is over an order of magnitude lower than any other measurements.

More recently Volkensteyn and Galoshina³ measured polycrystalline scandium from 4.2 to 300°K and reported a room temperature susceptibility of 5.08×10^{-6} emu/gram. They gave the following analysis in ppm by weight: H 20, O 340, N 160, Fe 300, Mo 100, Cu 400 and Ca 80. Their data are anomalous in that at approximately 40 °K it levels off at 7.75×10^{-6} emu/gram and remains linear to the lowest temperature measured. This is difficult to explain considering the large amount of iron reported above.

Samples of polycrystalline scandium from both Johnson Matthey & Co. and L. Light & Co. were measured from 10 to 293 °K by Gardner and Penfold.⁴ The total rare earth content was about 700 ppm by weight in the Johnson Matthey metal and about 1700 ppm by weight in the L. Light metal. The uncorrected data were remarkably similar for the two samples, namely 6.10

and 11.33×10^{-6} emu/gram at 300 and 10°K respectively. Using a collective electron band model, Gardner and Penfold⁴ estimated the various contributions to the total susceptibility at 0°K as follows: χ_i , the diamagnetic contribution of the scandium atoms, as $-.67 \times 10^{-6}$ emu/gram, χ_o , the orbital paramagnetism of the d band electrons, as 2.11×10^{-6} emu/gram, χ_p^e , the Pauli paramagnetism taking into account electron-electron interaction, as 5.45×10^{-6} emu/gram.

After zone refining the above metal from Johnson Matthey & Co., Anderson et al.⁵ reported a slight drop in the room temperature susceptibility and a significant drop at low temperatures. In addition a sample obtained from Bell Laboratories and purified by triple distillation, was measured and found to have a room temperature susceptibility approximately 10% higher than the Johnson Matthey sample. This sample also had very little upturn in the data at low temperatures, indicating a sample of relatively high purity with regard to magnetic impurities. The slope of the temperature dependence of χ was very nearly the same for all three samples and it was suggested that the difference in the data was due to gaseous impurities, structural effects or anisotropy in the polycrystalline samples.

In addition Kobayashi⁶ has measured polycrystalline scandium over the temperature range of 1.4 to 4.2°K and 14 to 20°K respectively. He found a susceptibility of 14.13 and 8.34×10^{-6} emu/gram at 4.2 and 20°K respectively. His data were in fair

agreement with the Johnson Matthey sample measured by Gardner and Penfold⁴ which was reported to contain over 700 ppm by weight of other rare earth impurities. To correct for 80 ppm (atomic) iron a correction ranging from 2.6×10^{-6} emu/gram at 4.2°K to 8.34×10^{-6} emu/gram at 20°K was subtracted from the measured values. No correction was made for rare earth impurities.

Kohlhaas and Weiss⁷ have also recently measured polycrystalline scandium. The susceptibility of their sample ranged from a low of 5.85×10^{-6} emu/gram at 290°K to a high of 9.02×10^{-6} emu/gram at 5°K. The sharp upturn at low temperatures indicates that their sample contained considerable magnetic impurities. No attempt was made to correct for these impurities which included .03 wt % iron. Gaseous impurities were not considered.

As with the polycrystalline specimens, the data from the previous single crystal measurements showed considerable scatter in the values of χ .

The susceptibility of single crystal scandium was measured by Chechernikov et al.⁸ in 1963. These measurements were carried out between 70-1100°K on metal with the following reported impurities in ppm by weight: $0 \leq 1100$, $C \leq 140$, $Mo \leq 60$, $N \leq 400$, $Ca \leq 200$ and $H \leq 89$. The data were found to obey the Curie Weiss law with $\theta_c = -1300^\circ K$ and $\theta_a = -900^\circ K$. The possibility of an antiferromagnetic exchange interaction was suggested to explain the negative sign of θ . The magnetic

susceptibility was found to be greater in the c direction than the a direction which is in disagreement with the most recently published data. It is interesting to note that Volkov et al.⁹ who supplied Chechernikov with his single crystals, also found anisotropy values of the resistivity of scandium which are reversed from those recently determined by Spedding et al.¹⁰

Chechernikov et al.¹¹ also measured polycrystalline scandium over the same temperature region and found that these data agreed reasonably well with the weighted average ($\chi_{\text{poly}} = 2/3\chi_a + 1/3\chi_c$) of the single crystal data. Likewise the data obeyed a Curie Weiss law with an effective moment and paramagnetic Curie temperature equal to $1.67 \mu_B$ and -1050°K respectively. The chemical analysis of this metal in ppm by weight was reported as follows: $\text{H} \leq 74$, $\text{O} \leq 1160$, $\text{N} \leq 400$, $\text{Cu} \leq 700$, $\text{Mo} \leq 20$ and $\text{Co} \leq 500$. No analysis was given for rare earth or transition metal impurities in either the single or polycrystalline specimens.

In 1968 Wohllleben¹² measured both single and polycrystalline scandium from .38 to 300°K and found χ_c greater than χ_a in agreement with Chechernikov. In addition he found that his polycrystalline data did not agree with the weighted average of the single crystal data, being somewhat lower than either the a or c axis and having a different temperature dependence. He speculated that this discrepancy was due to spin orbit scattering on dislocations and grain boundaries.

In order to correct for impurities in his samples Wohlleben used a differential susceptibility technique based on the method of Hondo¹³ and Owen.¹⁴ In using this technique he assumed that at .38°K the paramagnetic impurities were saturated and that the actual susceptibility could be obtained from the slope of a plot of moment vs magnetic field. The corrected data for scandium showed a decrease in the susceptibility at lower temperatures with a maximum at approximately 5°K. The actual data showed a sharp upturn at low temperatures. A number of polycrystalline samples obtained from different sources were measured at .38, 150 and 293°K and considerable scatter was observed in the data, ranging from 4.13 to 6.45×10^{-6} emu/gram at room temperature. Wohlleben speculated that this scatter was due to a suppression of the susceptibility by heavy nonmagnetic impurities via spin orbit scattering. This scattering was speculated to have lowered the susceptibility by decreasing the spin polarization of the conduction electrons. One atomic % of vanadium, niobium and tantalum in scandium was found to reduce the susceptibility by 1, 4.5 and 14.8% respectively. In addition Wohlleben found that dilute ScFe alloys showed the largest specific depression of the room temperature susceptibility of scandium, about 60% per atomic % iron.

Most recently Ross et al.¹⁵ measured both single and polycrystalline scandium from 4.2 to 300°K. In contrast to both Chechernikov and Wohlleben the susceptibility was found to be

greater along the a axis than the c. The polycrystalline data increased from 6.34 to 8.77×10^{-6} emu/gram between 300 and 4.2 °K and was found to agree well with the weighted average of the single crystal data. The magnetic anisotropy of three of the four single crystals measured was found to increase at low temperatures, being approximately .22, .29 and $.66 \times 10^{-6}$ emu/gram at 300, 25 and 4.2°K respectively. The anisotropy of the fourth crystal, however, showed a sharp decrease at low temperatures, the respective data being .20, .22 and $.11 \times 10^{-6}$ emu/gram at 300, 25 and 4.2°K. No reason for this discrepancy could be given except the possibility of some impurity effect. The analysis of these samples indicated a total rare earth concentration of approximately 125 ppm (atomic) and 100 ppm (atomic) iron. The analysis of gaseous impurities was not given.

In Figs. 10 and 11 in the Results section the temperature dependence of the susceptibility of scandium as reported by the various investigators is presented along with the results found in the present investigation.

Some work has also been carried out on the magnetic properties of scandium alloys containing known amounts of impurities. Isaacs et al.¹⁶ have shown that the effective moments of both Dy^{+3} and Gd^{+3} are enhanced in a scandium matrix, with the enhancement falling off rapidly with increased solute concentration. The enhancement of the effective moment of Dy^{+3} and Gd^{+3} in a .02 a/o alloy relative to that of the pure

metal was 1.68 and 1.38 respectively. They believed the enhancement was due to the magnetic polarization of the scandium matrix by the solute and it is felt that at extreme dilution the isolated solute atoms interact ferromagnetically, over a finite volume of material, with the spins of the solvent matrix. Due to overlapping of the polarization clouds, with subsequent cancellation effects, the moment of the solute falls off rapidly with increased concentration. Wohllleben¹⁷ has also found that the saturation moment of Gd^{+3} is enhanced above the free ion value by over 30% in a sample containing 76 ppm of the solute. He too felt that this increase in the impurity moment resulted from a ferromagnetic coupling of the spin of the partially localized d electron ($p_{eff} = 1.67 u_B$) with the impurity spins.

Several investigators have also reported susceptibility results of scandium metal containing dilute amounts of non-magnetic metallic impurities. Anderson et al.⁵ measured scandium containing 3, 5 and 10 wt % titanium at room temperature and found that the susceptibility was lower by approximately 1% per wt % solute. They interpreted this as resulting from a decrease in the density of states brought about by a rigid band shift of the Fermi level. More recently Isaacs et al.¹⁶ found that the addition of .2 at.% cerium and .5 at.% titanium increased the susceptibility of scandium while 2.0 at.% cerium decreased it. In light of this behavior they proposed that the Fermi energy lie just to the left of a peak in

the density of states curve. The rigid band shift of E_f upon alloying was speculated to first increase and then decrease the density of states, resulting in a corresponding change in the Pauli spin paramagnetism. Wohleben and Luo¹⁸ reported a general decrease in the room temperature susceptibility of scandium upon the addition of dilute amounts of supposedly tetravalent (Group IVB and thorium) and pentavalent (Group VB) elements. They speculated, however, that this behavior resulted from spin orbit scattering of the solute atoms. This interpretation resulted from a linearity which they observed between the decrease and the difference in the spectroscopic spin orbit energy between the host and solute atoms.

B. Yttrium

Although less work has been done on the determination of the magnetic properties of yttrium, there is somewhat better agreement between these results than with scandium. In 1939 Bommer¹ measured the susceptibility of polycrystalline yttrium over the temperature range 80 to 293°K. After correcting for 72 wt % KCl and various rare earth impurities, he found a room temperature susceptibility of 2.22×10^{-6} emu/gram which is in fair agreement with more recent data from considerably purer specimens.

Gardner et al.¹⁹ measured polycrystalline yttrium from two different sources and found that its susceptibility was

only slightly temperature dependent, the mean value falling from 2.20×10^{-6} emu/gram at 10°K to 2.09×10^{-6} emu/gram at 293°K . The yttrium samples were obtained from L. Light & Co. and H. J. Nolting²⁰ and were reported to have purities of 99.0 and 99.8 wt % respectively. The Nolting sample was prepared from oxide provided by the Ames Laboratory, Iowa State University and contained 20 ppm other rare earth impurities. Measurements made on these samples agreed within 3% over the entire temperature range with the L. Light sample having slightly higher values.

Using a collective electron band model, Gardner et al.¹⁹ estimated the various contributions to the total susceptibility in units of 10^{-6} emu/gram as follows: χ_i , the diamagnetic contribution of the yttrium atoms, as $-.39$, χ_o , the paramagnetic contribution due to the orbital angular momentum of the d band conduction electrons, as $.84$ and χ_p^e , the Pauli paramagnetism taking into account electron-electron interaction, as 1.74 .

More recently Gardner and Penford²¹ measured the metal supplied by Nolting over the temperature range 1.3 to 800°K . They found a maximum in the susceptibility at 300°K with the susceptibility falling linearly to 1.74×10^{-6} emu/gram at 800°K . They reported that this maximum would normally indicate the onset of antiferromagnetism but also pointed out that neutron diffraction and specific heat data do not reveal the occurrence of such a transformation.

Measurements on both single and polycrystalline yttrium

were carried out over the temperature range 90 to 300°K by Chechernikov et al.²² in 1964, but their samples apparently contained considerable impurities, the data showing a large temperature dependence and an unexplained anomaly at 170°K. More recently Chechernikov et al.²³ measured metal of much higher purity over the range 77 to 293°K. No anomalies were observed and the temperature dependence was much less, although the data still showed a slight increase as the temperature was lowered. This is in contrast to the data of Gardner and Penford²¹ which showed a slight decrease in the susceptibility at lower temperatures. Chechernikov reported that χ_a was larger than χ_c with an anisotropy of approximately $.13 \times 10^{-6}$ emu/gram. The room temperature values of χ_a , χ_c , and χ_{poly} were 2.20, 2.07 and 2.09×10^{-6} emu/gram respectively. The polycrystalline data did not agree with the weighted average of the single crystal values.

In 1968 a batch of yttrium from Nolting and previously measured by Gardner and Penfold was measured between .36 and 125°K by Wohlleben.¹² His measurements agreed well with Gardner and Penfold but using the differential susceptibility technique he found that the data actually decreased at low temperatures with a maximum between 2-3°K. Wohlleben also measured a number of polycrystalline yttrium samples from various commercial and private sources. At 4.2°K the susceptibility of these samples varied from a high of 110.24×10^{-6} emu/gram to a low of 2.10×10^{-6} emu/gram for the sample pro-

vided by Nolting. Wohllengenben also found that the susceptibility of yttrium could be lowered by adding nonmagnetic impurities. He observed a 3% lowering of the susceptibility of a second sample provided by Nolting after the sample, which was slightly contaminated with silicon vacuum grease, had been arc melted. No gaseous analyses were given however.

In Figure 27 of Section V the temperature dependence of the susceptibility of yttrium as measured by both Gardner and Penfold²¹ and Chechernikov et al.²³ are shown for comparison with the results found in the present investigation.

C. Lanthanum

The magnetic susceptibility of lanthanum was first measured by Trombe²⁴ who found a room temperature value of 1.2×10^{-6} emu/gram. More recently Lock²⁵ measured a predominantly double hcp sample of polycrystalline lanthanum and also found it to be paramagnetic with a temperature dependence approximately 1/3 that of scandium, its susceptibility falling from 1.5×10^{-6} emu/gram at 5.4°K to $.73 \times 10^{-6}$ emu/gram at 293°K. The difference of 60% in the room temperature values from the two investigations is believed to be due to the less pure samples used by Trombe.

Finnemore et al.²⁶ also measured a sample of double hcp polycrystalline lanthanum and found its susceptibility to be approximately 1×10^{-5} emu/gram at 4.2°K, a value nearly an order of magnitude higher than that previously reported. In addition

the susceptibility was found to be nearly independent of temperature, decreasing by only .3% as the temperature increased from 4.2°K to 78°K.

In 1968 Wohlleben¹² measured polycrystalline samples from five commercial sources and found a wide variation in both the measured susceptibility and its temperature dependence. The room temperature values of his purest samples agreed fairly well with Lock but exhibited less temperature dependence. This may be due to the presence of fcc phase since Wohlleben prepared his samples by annealing them for one month at 350°K, a temperature above the crystallographic transformation temperature of 310°C.

In Figure 32 of Section V the temperature dependence of the susceptibility of lanthanum as measured by both Lock²⁵ and Wohlleben¹² are shown for comparison with the results found in this investigation.

D. Lutetium

The only reported value of the susceptibility of lutetium metal was in a review book published in 1957. At that time Spedding et al.²⁷ reported a room temperature susceptibility of 1.023×10^{-7} emu/gram. However these authors feel that, due to a typographical error, this value should have read 1.023×10^{-6} emu/gram.^a

^aS. Legvold, Ames Laboratory, I.S.U., Ames, Iowa.
Private communication. 1972.

III. APPARATUS

A. Theory

Provided the region around the specimen is evacuated, the potential energy of a diamagnetic or paramagnetic body of permeability μ and mass m in a magnetic field is defined by

$$U = -m \frac{(\mu-1)}{8\pi} H^2 \quad (1)$$

When situated in a nonuniform field a force equal to

$$F_x = - \frac{dU}{dx} = m \frac{(\mu-1)}{8\pi} \left[\frac{d(H_x^2)}{dx} + \frac{d(H_y^2)}{dx} + \frac{d(H_z^2)}{dx} \right] \quad (2)$$

is exerted on the body, where x is the direction of nonuniformity of the magnetic field and hence the direction in which the body tends to move. The experiment is greatly simplified by designing the magnet pole pieces such that the first two terms of Eq. 2 are negligible. Expressions similar to Eq. 2 for the forces parallel to the y and z direction are likewise negligible although it must be emphasized that these forces are always present to some extent and can result in lateral motion of the sample, especially when measuring materials with large moments.

Since $\mu = 1 + 4\pi\chi$, χ being the susceptibility of the body, the force in dynes is equal to

$$F_x = 1/2 m \chi d \frac{(H_z^2)}{dx} \quad (3)$$

Thus by measuring the force exerted by the nonuniform field on

a body its susceptibility can be directly determined provided the force gradient $d(H_z^2)/dx$ is accurately known. It follows that the direction in which the body moves depends on the sign χ . If χ is positive the body will move in the direction of increasing field and hence is a paramagnet. On the other hand if χ is negative then the body is diamagnetic and will move in the direction of decreasing field.

It must be pointed out that Eq. 3 is correct only when the field is not distorted by the introduction of the body to be measured. Hence, unless a correction for the demagnetization factor is carried out, this method can be used only for materials having small permeabilities.

B. Apparatus

The Faraday apparatus used in this study is shown schematically in Fig. 1 and was capable of operating over a pressure range of 1 to 10^{-5} torr and a temperature range of approximately 1.5 to 300°K. The force exerted on the sample was measured with an electrobalance which was contained in a 8"x16" diameter stainless steel drum with a 3/4" aluminum plate bottom. This electrobalance was mounted onto an aluminum table which was adjustable in height, allowing proper leveling of the balance. The balance chamber had a 1/4" stainless steel lid, vacuum sealed with an "O" ring. In order to properly center the sample in the magnetic field the balance chamber was mounted on a milling table, fully movable in two perpendic-

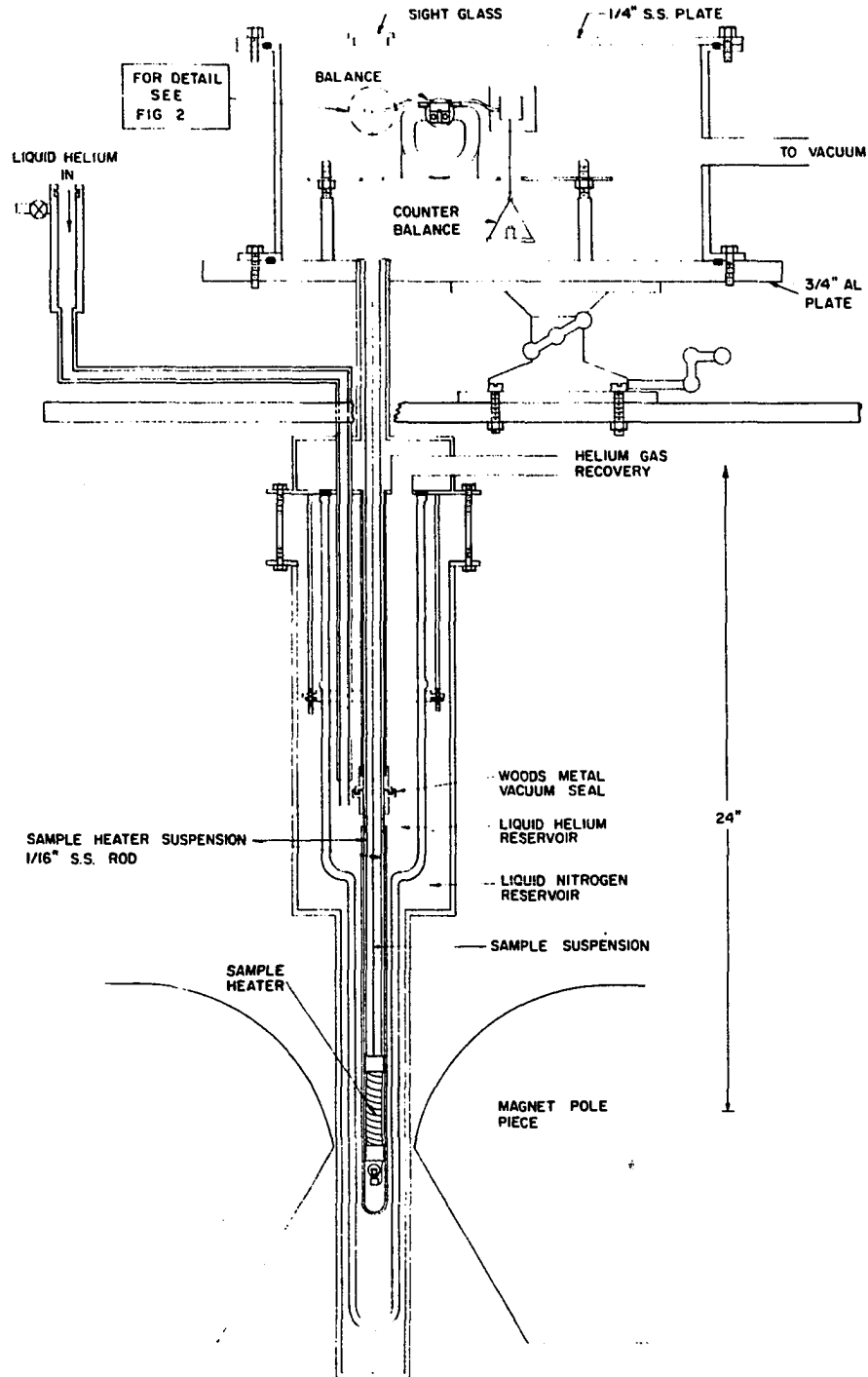


Fig. 1. Schematic diagram of the Faraday apparatus.

ular horizontal directions. The milling table was in turn mounted to a stainless steel plate which was positioned between the balance chamber and magnet. This plate, which measured 25" square by 1/2" thick, was made relatively massive for two reasons, (1) to provide an effective shield for the stray field of the magnet and (2) to dampen out mechanical vibrations. Threaded into the aluminum bottom of the balance chamber was a 1" diameter stainless steel tube from which the cryogenic system was suspended. The sample chamber consisted of a thin walled stainless steel tube with a detachable glass tailpiece, mounted with a standard woods metal seal. The sample chamber had a total length of 32".

The cryogenic system consisted of a glass helium dewar and a stainless steel nitrogen dewar, both of which were the standard variety. The nitrogen dewar measured 6" in diameter at the top and 2.3" at the bottom, the latter dimension being the magnet pole piece separation. Both dewars are shown in position in Fig. 1.

The temperature of the sample, via a small amount of helium exchange gas, was varied by a heater assembly consisting of a 3/4" O.D.x4" copper tube wound noninductively with 200 ohms of manganin wire. The entire heater assembly was suspended from the balance chamber with two 1/16" stainless steel rods. Both ends of this assembly were wrapped with Teflon tape to insulate it from the rest of the apparatus. This insulation also served to center the heater assembly in

the tailpiece. Current to the heater element was supplied simply by a DC power supply and a variable resistor in series with the heater. The temperature was controlled by hand by careful adjustment of the current to the heater element. Using this method it was found that the temperature could easily be maintained to within $\pm .05^{\circ}\text{K}$ at low temperatures and $\pm .1$ at higher temperatures.

The sample temperature was measured over the range 1.5 to 20°K with gold-.03% iron vs copper thermocouple and over the range 20 to 300°K with a constantan vs copper thermocouple. Since the thermocouples could not be placed in direct contact with the sample, they were bonded at midpoint to the inner surface of the copper tube with #7031 GE varnish. To check for temperature gradients along the length of the heater two additional thermocouple elements were positioned $1/2''$ on either side of the first thermocouple. No gradient was found within the experimental accuracy of the thermocouples.

Calibration of the middle thermocouple to $\pm .01^{\circ}\text{K}$ was carried out from 1.5 to 80°K with reference to a germanium resistance thermometer previously calibrated to $\pm .001^{\circ}\text{K}$ by Dr. Swenson's Physics group. The calibration was carried out by suspending the germanium crystal inside the heater in the same position as the sample, i.e. at the midpoint of the copper tube. Since the germanium crystal had not been calibrated above 80°K , a linear extrapolation was carried out between 80°K and room temperature. A plot of emf vs tempera-

ture had the same slope from room temperature to well below 80°K. The outer two thermocouples, although not directly calibrated, were assumed to have the same calibration as the middle one since they were all prepared from the same roll of thermocouple wire.

1. Electrobalance

The force exerted on the sample was measured with an RH Cahn electrobalance purchased from the Cahn Instrument Company. This balance had a sensitivity of 10^{-6} grams and a precision of .01% of the range of the weight change. It was capable of weighing specimens of up to 100 grams and weight changes of up to 20 grams. The entire balance system consisted of the electrobalance, recorder and control unit. The control unit in turn consisted primarily of a precision potentiometer.

The electrobalance operated on the well known null balance technique. When the sample weight changed the momentary deflection of the balance beam resulted in a corresponding change in the amount of light entering a phototube. This is carried out by means of a flag attached to the balance beam and positioned between the phototube and light source. The current from the phototube was amplified in a two-stage servo amplifier and fed to the balance beam coil which was positioned in a permanent magnetic field. This current restored the beam to the original balance position. Since by Amperes Law, the electromagnetic restoring force is exactly proportional to the current which caused it, the change in current in the coil is

proportional to the change in weight of the sample. Thus by accurately measuring this current the weight change of the sample could be directly determined. In order to use a practical recorder, a known accurately calibrated voltage was first subtracted from the total voltage by means of the precision potentiometer. The excess of coil voltage over that subtracted was then displayed on the chart recorder. Both the potentiometer and the recorder were calibrated to read directly in milligrams. Thus the total weight change was the sum of that subtracted by the potentiometer plus the recorder reading. By adjusting the voltage to the potentiometer by precise amounts various weight ranges could be measured.

2. Sample suspension

In order to measure the magnetic anisotropy in both single and polycrystalline samples it was necessary to build a rigid suspension to prevent rotation of the samples in the magnetic field. After a number of failures, the suspension shown schematically in Fig. 2 was built and gave excellent results throughout the course of the investigation.

This suspension consisted of a double hook arrangement built from No. 22 copper wire and used two tapered brass 0-80 screws for knife edges. The double hook was attached rigidly to a 1 mm quartz rod measuring roughly 36" in length. Quartz was used because its susceptibility is small and relatively constant with temperature thus keeping the correction for the

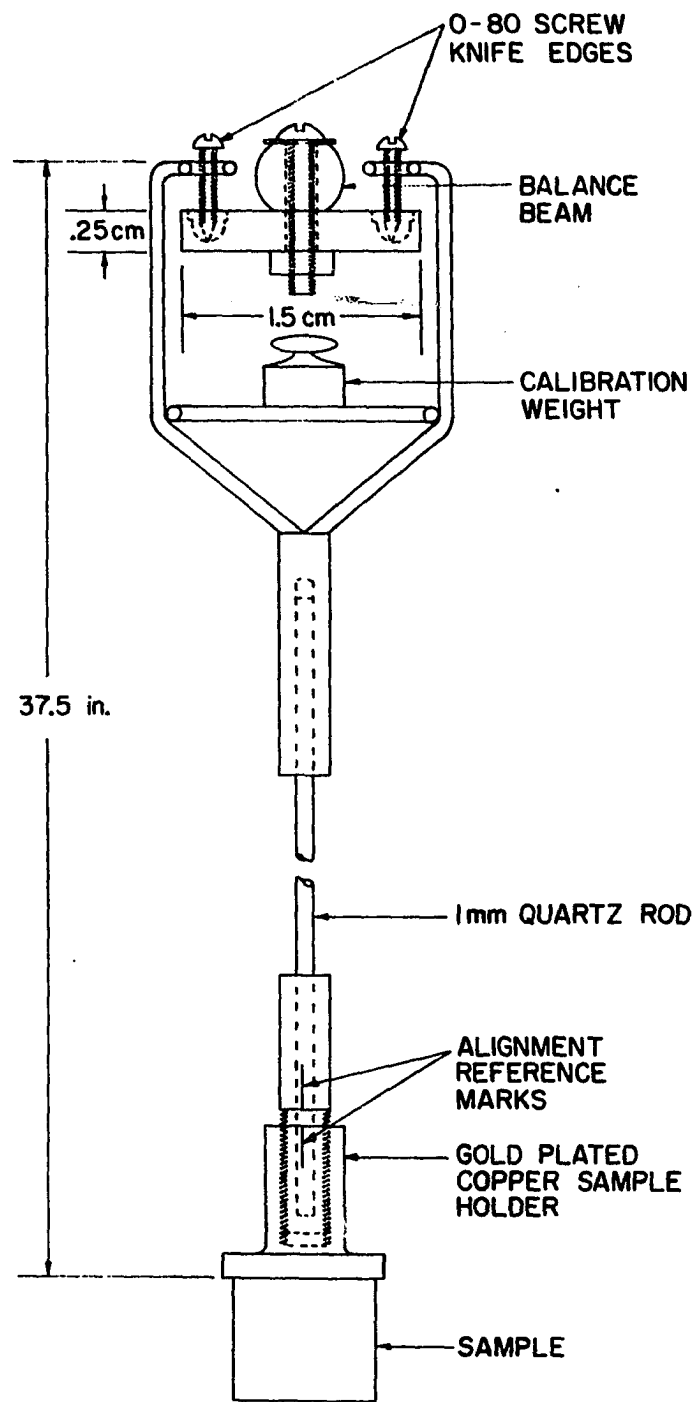


Fig. 2. Schematic of the rigid sample suspension used to measure the magnetic anisotropy.

suspension to a small and fairly constant part of the total susceptibility. In addition quartz has a low coefficient of thermal expansion which enables the suspension to be used without fear of displacing the sample from the volume element over which $d(H_z^2)/dx$ is a constant as the temperature of the apparatus is lowered.

The sample holder itself was threaded to a sleeve which was in turn attached to the quartz rod. This enabled the sample holder to be easily demounted from the sample suspension. The sample holder had a plane surface, perpendicular to the quartz rod to which the samples were affixed with a small amount of GE varnish. Both the sample holder and sleeve were made from copper and protected by a gold plate to insure a constant susceptibility during the course of the investigation.

The double hook suspension was hung from the balance beam by means of a copper cross bar containing two cups for receiving the knife edges. These cups had rounded bottoms which were machined with a 1/16" ball mill and smoothed by firmly pressing a 1/16" stainless steel ball against the bottom of the cups. This operation was repeated, after first etching the worked surface with dilute nitric acid, until the rounded surfaces appeared smooth under a 100X magnification.

In developing the final design for this suspension it was found that only with the rounded bottom in the cups was good reproducibility in the force measurements attained. Initially both a tapered and flat surface was tried but erratic behavior

was observed. In addition it was found that the suspension worked best with the cross beam fastened to the bottom rather than the top of the balance beam.

3. Magnetic field gradient

Inherent in the Faraday technique is the magnetic field gradient required to produce a measurable force on the sample. As shown by Eq. 3 this force in dynes is proportional to $d(H^2)/dx$. Thus in order to be able to measure different specimens of arbitrary size and shape it is necessary to produce a relatively constant field gradient over a usable sample volume. Otherwise excessive time would be consumed in calibrating the apparatus, as this would involve a comparison of each specimen with a standard material occupying the identical volume. Therefore the pole pieces used in this investigation were designed to produce a relatively large volume element over which $d H^2/dx$ is a constant.

The surface specification for the pole pieces which were used in this investigation were calculated by Dr. R. Jordan following a method developed by Garber et al.²⁸ and Heyding et al.²⁹ These pole pieces, shown in Fig. 3 are 11" in diameter and were machined from soft iron. The curved surfaces have been replaced by straight line segments in order to facilitate machining.

The magnet was a 100 kw Arthur D. Little oil cooled laboratory electromagnet. This magnet could be raised or lowered 18 inches and rotated 360°, 180° in either direction from the

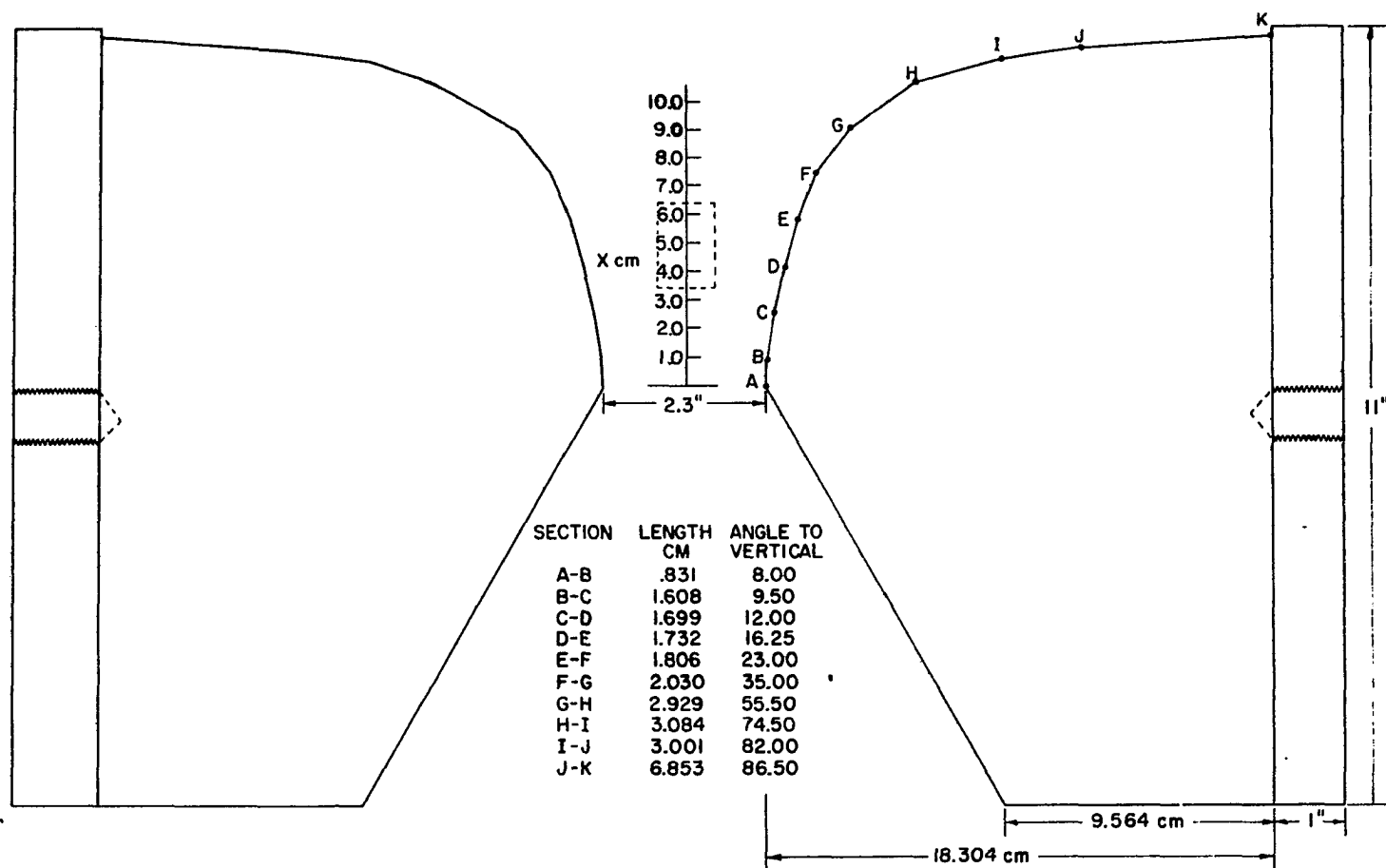


Fig. 3. Cross section profile and specifications of the pole pieces. The rectangular shaped area enclosed by the broken line is the sample position.

normal position. The magnet power supply regulated the current to the magnet to a few parts in 10^5 .

In order to determine the field characteristics of the pole pieces, the magnetic field was measured as a function of sample depth with a rotating coil gaussmeter which had previously been calibrated by means of an nmr experiment. Plots of H^2 vs x , the sample depth, for several current settings are shown in Fig. 4. It is observed that from approximately 3.3 to 6.4 cm the slopes of the curves are linear, indicating a constant field gradient.

Calibration was carried out by a relative method based on the accepted susceptibility of $-.168 \times 10^{-6}$ emu/gram for triply distilled mercury. Mercury was chosen because of its widely accepted value and because it was readily available in high purity. The field gradient constants calculated from the force exerted on such a sample are listed in Table I. Using these values the susceptibility of a high purity lead sample, obtained from Mr. John Greiner, was measured and good agreement was observed between his value and mine, $-.1123 \times 10^{-6}$ emu/gram and $-.1117 \times 10^{-6}$ emu/gram respectively. His apparatus had recently been calibrated using high purity water. The susceptibility of this lead sample, measured at the eight field settings for which the apparatus was calibrated, are listed in Table I and show a mean deviation of .13%.

A sample of high purity platinum was also measured at the eight field values. These values are also listed in Table I

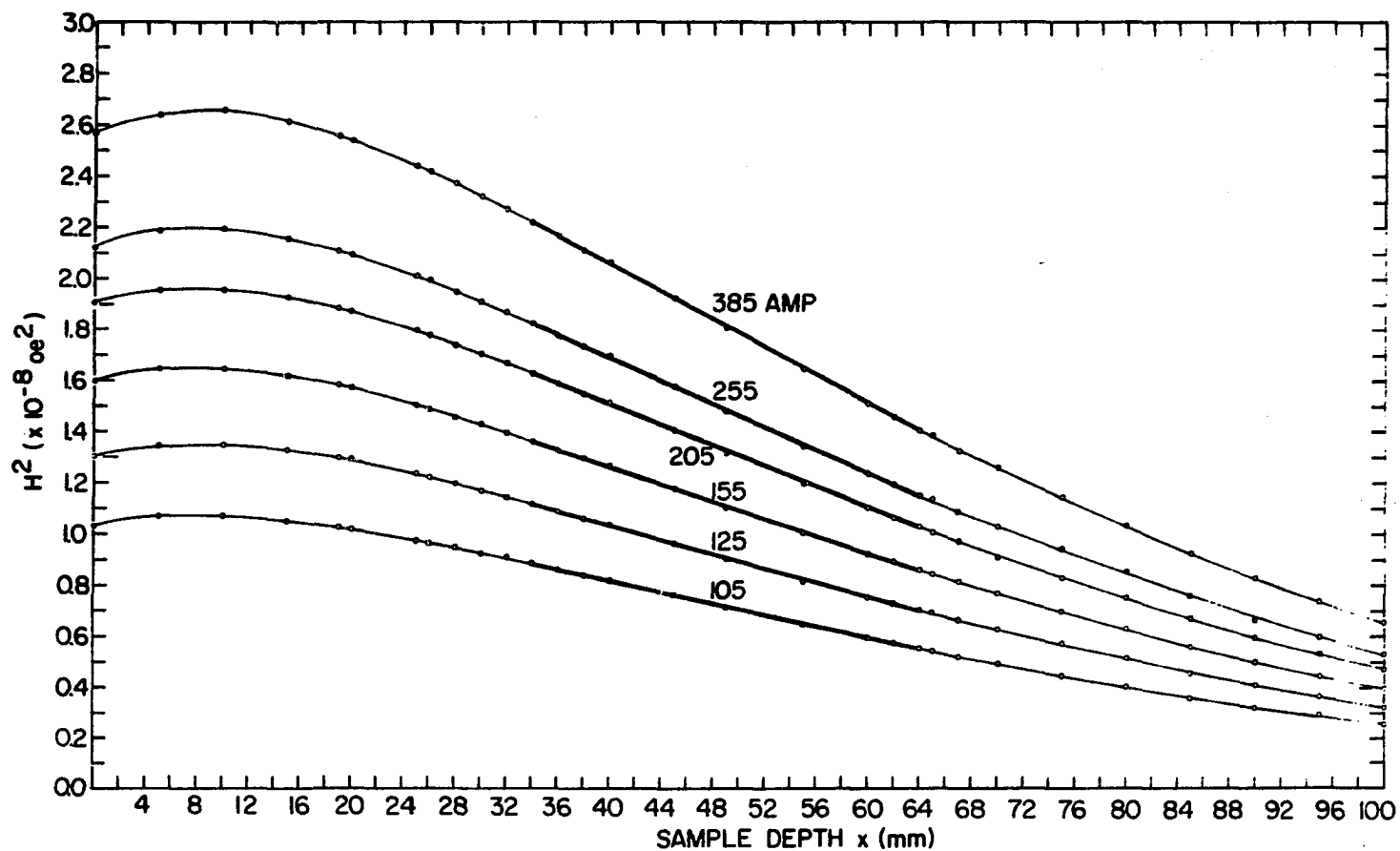


Fig. 4. Plots of H^2 (Oe^2) versus sample depth at six amperage settings. The linear portion of these curves, shown by the heavy lines, indicate regions over which the field gradient $d(H^2)/dx$ is a constant.

Table I. Field gradient constants and the susceptibility of high purity lead and platinum

Current (amps)	Field (gauss)	Field gradient constants ($\times 10^{-6}$ gauss ² /cm)	χ ($\times 10^{-6}$ emu/g)	
			Pb	Pt
385	13540	26.925	.1122	1.0101
305	12802	24.181	.1124	1.0088
255	12250	22.278	.1121	1.0098
205	11555	19.903	.1124	1.0093
175	11012	18.110	.1124	1.0104
155	10545	16.652	.1123	1.0078
125	9503	13.504	.1124	1.0105
105	8408	10.574	.1125	1.0100

and show a mean deviation of less than .1%. The average value of the sample agreed well with the most recent value reported in the literature, namely 1.0150×10^{-6} emu/gram.²⁹

The optimum sample position was found by raising and lowering the magnet while measuring the force on the mercury sample. These force measurements were found to be constant over a range only slightly less than 3 cm.

IV. EXPERIMENTAL PROCEDURE

A. Sample Preparation

1. Metal preparation

Several batches each of scandium, yttrium, lanthanum and lutetium metal were prepared from the highest purity oxides available from Dr. Powell's Ion Exchange group. All of the metals were prepared via the calcium reduction of the fluoride salt. The calcium was purified by triple distillation and contained on the average 60 ppm oxygen, 100 ppm hydrogen, <5 ppm nitrogen and 40 ppm carbon, all in ppm by weight. With the exception of ScF_3 , the fluorides were prepared by heating the rare earth oxides at 600°K in a stream of anhydrous HF followed by a topping treatment in which the salts are melted in an atmosphere of HF. Both of these operations were carried out in a platinum boat and resulted in a final product containing approximately 10 ppm oxygen by weight. Due to its volatility at its melting point, ScF_3 was prepared by the low temperature operation only and hence contained more oxygen in the as reduced metal. However this had little effect on the final metal since oxygen is relatively easy to remove from scandium by a low temperature sublimation. The preparation of these fluorides is described in detail by Henderson.³⁰ Purification of the metals was carried out by either vacuum melting or vacuum melting followed by sublimation or distillation into a tungsten condenser. The techniques involved are described in

detail elsewhere.^{31,32}

2. Preparation of single crystal specimens

Single crystal specimens of scandium, yttrium and lutetium were prepared from arc melted billets by a strain anneal method similar to that described by Nigh.³³ In the present case, however, the arc melted billets were hung inside a well outgassed tantalum crucible which was then sealed under approximately a half atmosphere of helium gas. This method results in considerably less sublimation of the metal during crystal growth and less contamination from gaseous impurities than if the samples were simply hung in an open vacuum.

The crucibles containing the samples were hung in a 10^{-9} torr vacuum furnace and heated to a temperature approximately 100°C below the melting point of the metal or in the case of scandium and yttrium approximately 100°C below the high temperature allotropic transformation temperature. This temperature was maintained from 24 to 36 hours and then cooled over a period of several hours to room temperature.

After aligning to within $1/2^{\circ}$ with a Laue X-ray camera the grown crystals were cut perpendicular to the crystallographic axis by spark cutting. The alignment of the cut crystals was rechecked after first electropolishing them in a solution of 10% perchloric acid and methanol at -78°C .

3. Attempts to grow lanthanum single crystals

Due to the low fcc-dhcp transformation temperature in lanthanum the strain anneal technique³³ could not be used to

grow single crystals of this element. Therefore attempts were made to grow crystals by the molten zone^{34,35,36} and the crystallographic transformation³⁶ techniques.

The molten zone method entails the passage of a molten zone slowly along the length of a rod of the material under investigation. Single crystals of almost all the heavy rare earths^{34,35} have been grown in this manner. Recently Tonnie and Gschneidner³⁶ used this technique to grow crystals of both neodymium and praseodymium. However when such an operation was carried out on two 50 gram rods of lanthanum only small crystals were formed, as verified by extensive Laue X-ray investigation.

The crystallographic transformation method proved to be equally unsuccessful in growing single crystals of lanthanum. This technique is carried out by cycling the metal under consideration a short distance above and below its transformation temperature. Recently it was used successfully to grow crystals of both neodymium and praseodymium³⁶ and it was felt that it might possibly work for lanthanum, despite its much lower transformation temperature. One of the 50 gram rods from above was bisected and both sections sealed under 2/3 atmosphere of argon in a well outgassed tantalum crucible. These crucibles were in turn sealed in quartz capsules. The one sample was given an anneal for 45 days at 285°C while the second was cycled daily between 285°C and 340°C for 30 days followed by an anneal for 15 days at 285°C. The cycle con-

sisted of an anneal for 22 hours at 285°C and a two hour anneal at 340°C. After removing from the furnace both samples were extensively investigated by Laue X-ray technique and no crystal growth was detected, the bulk of the pictures showing a discernible ring like pattern generally associated with powder patterns. This investigation, though not extensive, seems to verify that self diffusion in lanthanum is extremely low below 310°C, thus preventing any reasonable growth rate in the specimen.

4. Preparation of polycrystalline specimens

Due to the considerable anisotropy remaining in arc melted specimens of yttrium and lutetium a recrystallization process was carried out to increase the randomness in the polycrystalline specimens. After arc melting, the samples were rolled approximately 20% and recrystallized for 24 hours at 725°C and 675°C for yttrium and lutetium respectively. In the case of yttrium this heat treatment reduced the anisotropy in these specimens from roughly 15% of the single crystal value to 2 or 3% in the best cases. The anisotropy was measured by rotating the sample in the magnetic field and observing the maxima and minima in the susceptibility. For lutetium the anisotropy in the arc melted samples was as high as 40% of the single crystal value. Recrystallization reduced this to values ranging from 1 to 7%.

The data available from these recrystallization studies indicate that although the samples recrystallized for 24 hours

at lower than the optimum temperature had a finer and more uniform grain structure, they still had considerable anisotropy. Apparently this was because the bulk of the recrystallized grains had the same directionality as their parents. Similarly samples recrystallized at higher temperatures also had considerable anisotropy, apparently due to too much grain growth. Shown in Figs. 5 through 8 are representative photomicrographs of lutetium samples in the arc cast as well as those recrystallized at 600°C, 675°C and 735°C. The amount of measured anisotropy in these samples was 41%, 26%, 1% and 24% of the single crystal value.

In the case of scandium no recrystallization was found to be necessary, the anisotropy being roughly 2 to 6% of the single crystal value in their arc melted state.

Hydrogenization was carried out by heating the samples to 550°C in a partial atmosphere of pure hydrogen gas. The samples were annealed at this temperature for 36 to 48 hours to insure homogenization. The apparatus used was a modified version of one described by Belle et al.³⁷ Polycrystalline samples of yttrium and lutetium were recrystallized prior to their hydrogenization.

The samples which were doped with oxygen, tantalum, titanium, iron and other rare earths were prepared by arc melting the samples with the stoichiometric amounts of the desired impurity. The lower concentration gadolinium and erbium alloys were prepared using the .1 a/o alloys as masters. To minimize

Fig. 5. Polarized light photomicrograph of arc cast lutetium metal. Specimen was found to have magnetic anisotropy equal to 41% of the single crystal value. 100X.

Fig. 6. Polarized light photomicrograph of lutetium metal recrystallized at 600°C. Specimen was found to have magnetic anisotropy equal to 26% of the single crystal value. 100X.

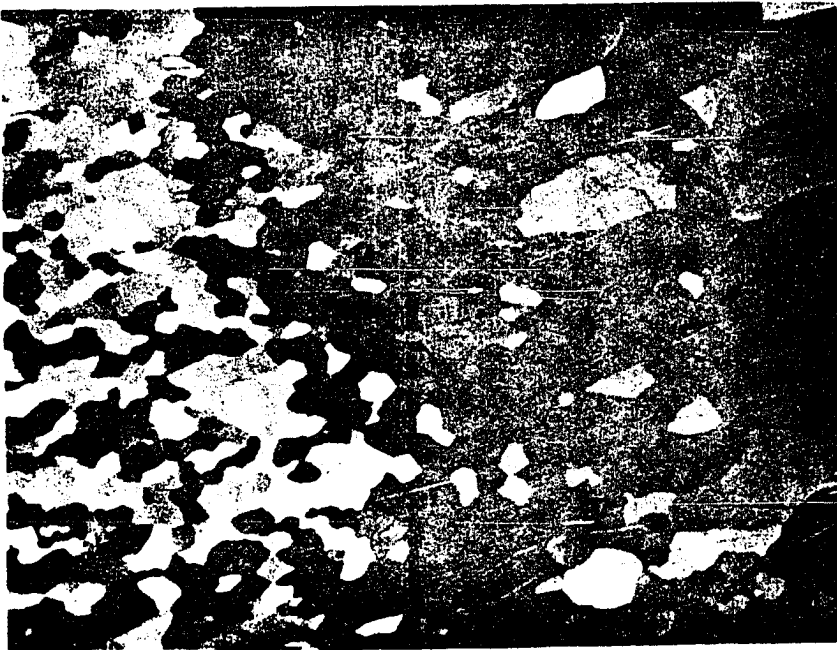
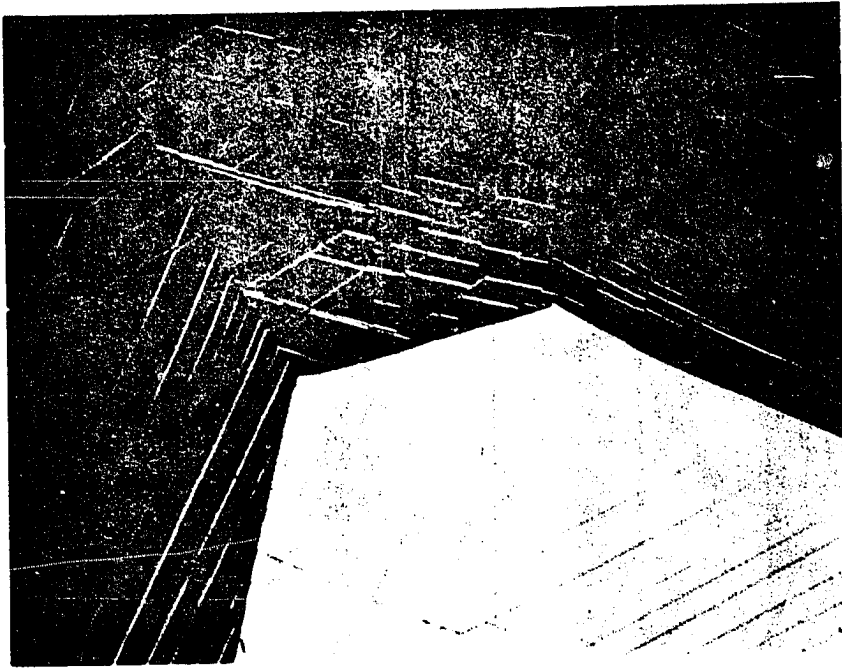


Fig. 7. Polarized light photomicrograph of lutetium metal recrystallized at 675°C. Specimen was found to have magnetic anisotropy equal to 1% of the single crystal value. 100X.

Fig. 8. Polarized light photomicrograph of lutetium metal recrystallized at 735°C. Specimen was found to have magnetic anisotropy equal to 26% of the single crystal value. 100X.



error resulting from a disproportionate loss of one of the constituents while melting, the arc was maintained at fairly low power. This was especially true for the scandium-erbium alloys since erbium has a slightly higher vapor pressure than scandium. Preferential loss of gadolinium during the arc melt would be very unlikely since its vapor pressure is an order of magnitude lower than that of scandium. Several of these specimens, weighed before and after arc melting, were found to lose only .1 to .2 w/o of the sample. To prevent contamination all of the constituents, with the exception of the rare earth oxides, were carefully electropolished prior to being arc melted. A pair of platinum tipped tweezers was used to hold the samples while electropolishing. Recrystallization of these samples was carried out in the same manner as the pure specimens.

Polycrystalline double hcp lanthanum samples were prepared by first swaging 3/8" arc melted rods 20% followed by an anneal at 450°C for five hours to bring about recrystallization. The temperature was then dropped to room temperature for 15 minutes and then set at 265°C for 10 days. The final samples were shown by X-ray analysis to be at least 90% hexagonal phase since no fcc phase was observed in the X-ray patterns. These patterns were taken using a polycrystalline wire technique described by Spedding and Beaudry.³⁸ Anisotropy remaining in the dhcp samples was the lowest of any of the samples measured, namely 1 to 2%.

B. Susceptibility Measurements

1. Sample positioning

The single and most of the polycrystalline specimens were measured by first affixing them to the sample holder, shown in Fig. 2, with a small amount of #7031 GE varnish. Since this surface was perpendicular to the quartz sample rod, the alignment of the vertical crystallographic axis was to within the same accuracy that the crystal itself could be aligned and sectioned. This is believed to be better than 1° . Prior to being placed in the sample chamber the single crystal specimens were aligned with the crystallographic direction to be measured roughly parallel with the magnetic field. This was carried out with the aid of several predetermined reference marks on the sample holder. These reference marks consisted of a scribe mark across the bottom of the sample holder along which the face of the cut crystal was aligned. In addition there are several marks on the two sections of the sample holder which, when aligned, indicate that the scribe mark is either parallel or perpendicular to the magnetic field. Once aligned the two sections of the sample holder were glued together with a small dab of GE varnish to prevent rotation of the sample in the field. After lowering the sample into the sample chamber a final and more accurate alignment was carried out by rotating the magnet until either a maximum or minimum was observed in the force measurements. In this manner it was believed that the samples could be aligned to within 1 to 2° .

All specimens were positioned in the magnetic field with their centers at a point 4.9 cm above the reference mark on the pole piece as shown in Fig. 3. Correct vertical positioning was carried out by measuring the distance from a reference point on the sample suspension to the center of the sample. After positioning in the sample chamber the reference mark on the sample suspension was used to center the sample at the 4.9 cm level by raising or lowering the magnet. The magnet could be positioned to within $\pm .01$ cm. Using a cathetometer accurate to $\pm .005$ cm, the sample could thus be positioned within an error of less than $\pm .02$ cm.

The samples were centered in the heater by visual observation through a sight glass in the lid of the sample chamber. A small light bulb positioned at the bottom of the heater provided the necessary illumination. The sample could be moved horizontally by adjusting the two knife edges, i.e. the two tapered 0-80 screws, in the sample suspension.

2. Force measurements

After first taring the constant part of the total load to ± 1 mg to achieve maximum sensitivity, the sample chamber was evacuated to approximately 10^{-5} torr. A small amount of helium gas was then introduced to provide thermal contact between the heater assembly and the sample. The weight change of the samples, read directly from the chart recorder and the mass dial of the balance control unit, was measured to the nearest 10^{-5} gram.

Measurements between 300°K and liquid nitrogen temperature were made during the slow cool down of the dewar and between 4.2 and 70°K by heating on the sample. Measurements below 4.2°K were made by pumping out the liquid helium reservoir. Temperatures as low as 1.5°K were obtained in this manner. The sample chamber was maintained at a constant temperature until thermal equilibrium was attained in the sample, as evidenced by a steady trace on the recorder. To insure that the magnetic field was the same for each reading, the voltage across the magnetization coils of the magnet was measured with a potentiometer.

Due to a slight drift in the balance reading when changing the sample temperature, the recorder was zeroed between measurements at different temperatures. This drift was especially pronounced at low temperatures and was believed to result from convection currents set up by the temperature gradient between the sample chamber wall and the heater assembly. Since the recorder was zeroed, the slight buoyancy resulting from these currents is not believed to have any effect on the accuracy of the measurements. Prior to zeroing the recorder and magnet current was set at zero for approximately 30 seconds for the residual field to die out.

3. Field dependence measurements

Since the specific force due to ferromagnetic impurities is greater by a factor of 10^{+4} to 10^{+6} than those of di or paramagnetic materials, trace amounts of these impurities can

lead to significant error in materials having small susceptibilities. For this reason all specimens were examined for a field dependence to determine if either ferromagnetism or saturated paramagnetism was present. This was carried out by using the method of Honda¹³ and Owen¹⁴ which assumes that in a strong magnetic field (>7000 gauss) the total moment of an impure material of unit mass is

$$M(T,H) = \chi H(T) + c\sigma(T,H) \quad (4)$$

Here the moment of a di or paramagnetic body is χH while that of a ferromagnetic or saturated paramagnetic body is $c\sigma$, c being the concentration of an impurity with saturated moment σ . From a plot of $M(T,H)$ vs H we obtain a slope equal to χ , the susceptibility and an intercept of $c\sigma$, from which a general idea of the purity of the sample can be obtained. In this investigation all of the samples except part of those specifically doped with impurities, were measured at the eight field values listed in Table I. The slopes and intercepts were calculated using a computer. In general these field dependent measurements were carried out at low temperatures only since it was found that very few of the samples exhibited any field dependence above liquid helium temperature unless the sample had been doped with relatively large amounts of iron or rare earth impurities. Also the data was not used to correct for impurities as is frequently the case, but only to determine the relative purity of the samples. Attempts to correct for

impurities by this method were fruitless since even at the lowest temperatures the bulk of the impurities behaved paramagnetically.

C. Methods of Analysis

Analyses of all the samples for oxygen, hydrogen and nitrogen were carried out by vacuum fusion methods.³⁹ The approximate detection limits for 0.5 gram samples are listed in Table II along with the precision for samples containing approximately those impurity levels listed. The precision for hydrogen results is not known but is believed to be of the same order of magnitude as oxygen and nitrogen for samples containing 10 ppm hydrogen by weight.

Table II. Detection limits and precision for analysis of O, H and N in rare earth metals by vacuum fusion analysis. Values are in ppm by weight.

Impurity	Detection limit	Precision	Impurity level
O	10 ppm	7%	150 ppm
H	0.5 ppm		
N	5 ppm	9%	100 ppm

Analyses for carbon, fluorine, iron and nickel were carried out by either conductometric or spectrophotometric techniques.^a The detection limits, precision and method used

^aR. Bachman, Ames Laboratory, I.S.U., Ames, Iowa.
Private communication. 1972.

are listed in Table III.

Table III. Analytical capabilities for the determination of typical impurities in the rare earths by wet chemical methods.

Element	Method	Detection limit ^a (ppm/1 g. sample)	Precision of value received (ppm by weight)
C	Conductometric	10	1% or 3 ppm
F	Spectrophotometric	5	2% or 2 ppm
Fe	Spectrophotometric	0.5	1% or 0.5 ppm
Ni	Spectrophotometric	2	2% or 1 ppm

^aDetection limits calculated for 0.1 gram samples are multiplied by ten for limit in ppm.

All other elements, including other rare earths, were analyzed by mass spectrograph analysis.^a The results for rare earth impurities are believed to have an absolute accuracy of +20% or less in the 1 ppm range. For nonrare earth metallic impurities the uncertainty is believed to be +300%. The difference in the accuracy between the rare earth and non-rare earth analyses results from the use of calibrated rare earth standards.

^aR. Conzemius, Ames Laboratory, I.S.U., Ames, Iowa.
Private communication. 1972.

V. RESULTS

A. Scandium

1. Sample purity

Four single crystals, designated 4-144,^a 4-155-A, 4-155-B and 4-160, were prepared from three separate batches of metal. The analyses of these crystals are listed in Table IV with all impurities listed in ppm atomic. Any impurity not listed was found to be present in a concentration of less than 1 ppm atomic. Since all of the polycrystalline specimens were prepared from unused portions of the billet used to grow the single crystals, these specimens were assumed to have the same analysis and are given the same numerical designation as the corresponding single crystal.

In order to assess their relative purity, all of the specimens were measured for a field dependence at several temperatures. Three of these magnetization curves shown in Fig. 9 show polycrystalline samples 4-155 and 4-160 to be almost completely free of any field dependent magnetism. Similar behavior was found for sample 4-144. Also shown in Fig. 9 is the magnetization curve for a sample known to contain over 100 ppm of various rare earth impurities, notably 30 ppm gadolinium, and 80 ppm iron. The susceptibility of this sample exhibited a field dependence below 10°K with a moment of .016 emu/gram at 1.45°K. If we assume for the sake of argument

^aCorresponds to Ames Laboratory notebook and page number.

Table IV. Analysis of scandium metal in ppm atomic.

Element	4-144	4-155	4-160	Element	4-144	4-155	4-160
H	175(4) ^a	357(8)	227(5)	Cu	16	<u><10</u>	6
C	386(103)	146(39)	220(59)	Y	2.2	4.5	2.5
N	22.5(7)	1.8(.5)	38(12)	La	.64	1.2	9.6
O	393(140)	129(46)	379(135)	Ce	<u><8</u>	1.6	.4
F	<u><10</u> (<u>4</u>)	33(14)	900(380)	Pr	<u><.45</u>	.64	.3
Na	20	3	8	Nd	<u><.8</u>	<u><.5</u>	<u><.4</u>
Mg	2	<u><.4</u>	<u><1</u>	Sm	<u><.2</u>	<u><.2</u>	.3
Al	1	2	<u><3</u>	Eu	<u><.08</u>	<u><.08</u>	<u><.4</u>
Si	4	<u><6</u>	<u><2</u>	Gd	<u><.5</u>	<u><2.0</u>	1
Cl	9	4	7	Tb	<u><.4</u>	0.3	.8
Ca	2	1	15	Dy	1.2	2.6	3.9
Ti	<u><2</u>	0.1	<u><.5</u>	Ho	.63	.6	1
V	<u><.2</u>	<u><.08</u>	<u><.1</u>	Er	1.7	1.2	.9
Cr	10	3	7	Tm	.06	<u><.1</u>	.1
Mn	.7	.2	4	Yb	.4	<u><.2</u>	<u><.3</u>
Fe	16	19.3	9.7	Lu	.5	1	2.5
Co	<u><.2</u>	<u><.6</u>	<u><.6</u>	Ta	6	3	3
Ni	6.0	10.7	3.8	W	20	20	2

^aPpm by weight.

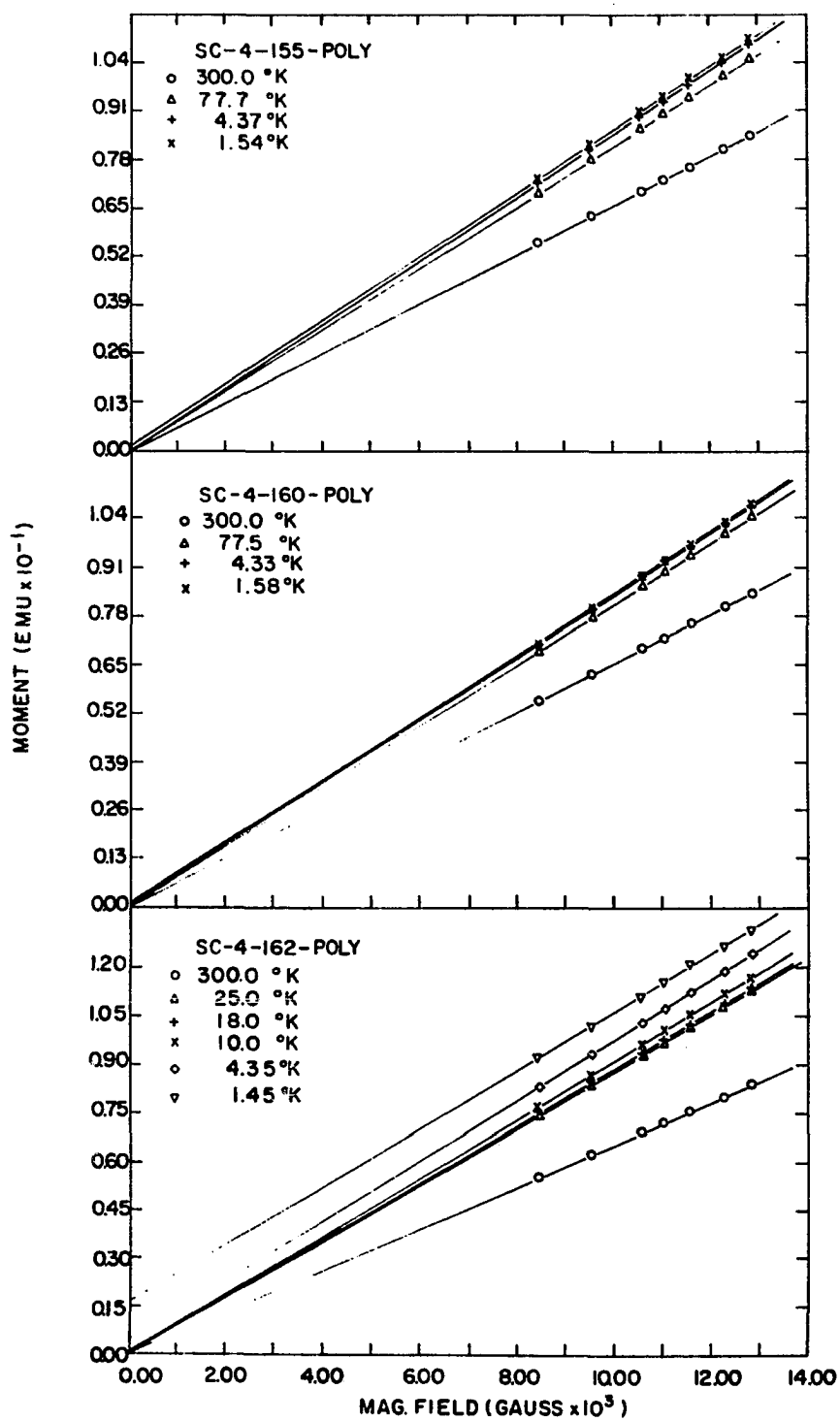


Fig. 9. Plots of magnetic moment versus field for several polycrystalline scandium samples.

that the only impurity present is gadolinium, having a saturation moment of 268 emu/gram, then this moment can be accounted for by 60 ppm.

2. Susceptibility of pure scandium

The susceptibility of the purest polycrystalline and single crystal specimens (4-155) are shown in Figs. 10 and 11. Also shown for comparison are the results of a number of previous investigations. For reasons of clarity the single and polycrystalline data are shown separately. The results for metal 4-155 are also shown in Fig. 41 along with that found in this investigation for yttrium, lanthanum and lutetium.

As noted, the room temperature susceptibility of Sc-4-155 was found to be the highest reported. Except at the lowest temperatures, however, the temperature dependence was approximately the same as that reported in several recent studies. A previously unreported maximum was found at 30°K which is especially marked for the "c" axis data. Below this temperature the data decreased until roughly 5°K where it again increased slightly. This final increase was especially evident in the polycrystalline and "a" axis data and is believed due to the presence of paramagnetic impurities. The fact that this upturn is much less than that reported at the same temperature in past studies indicates that the metal used in this study contained significantly fewer of these impurities.

For all of the single crystals, the susceptibility along the "a" axis was greater than that along the "c" axis which is

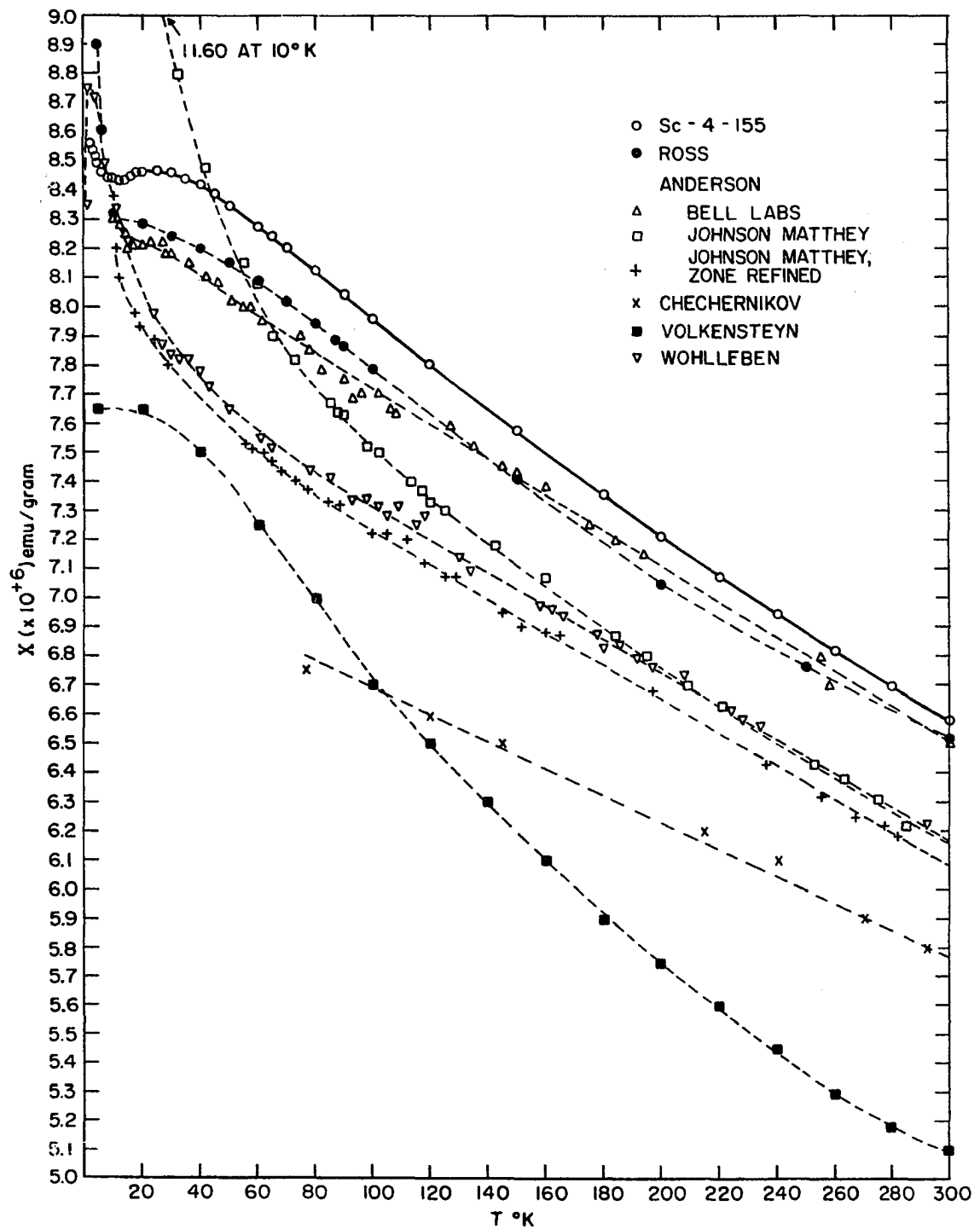


Fig. 10. Magnetic susceptibility of polycrystalline scandium.

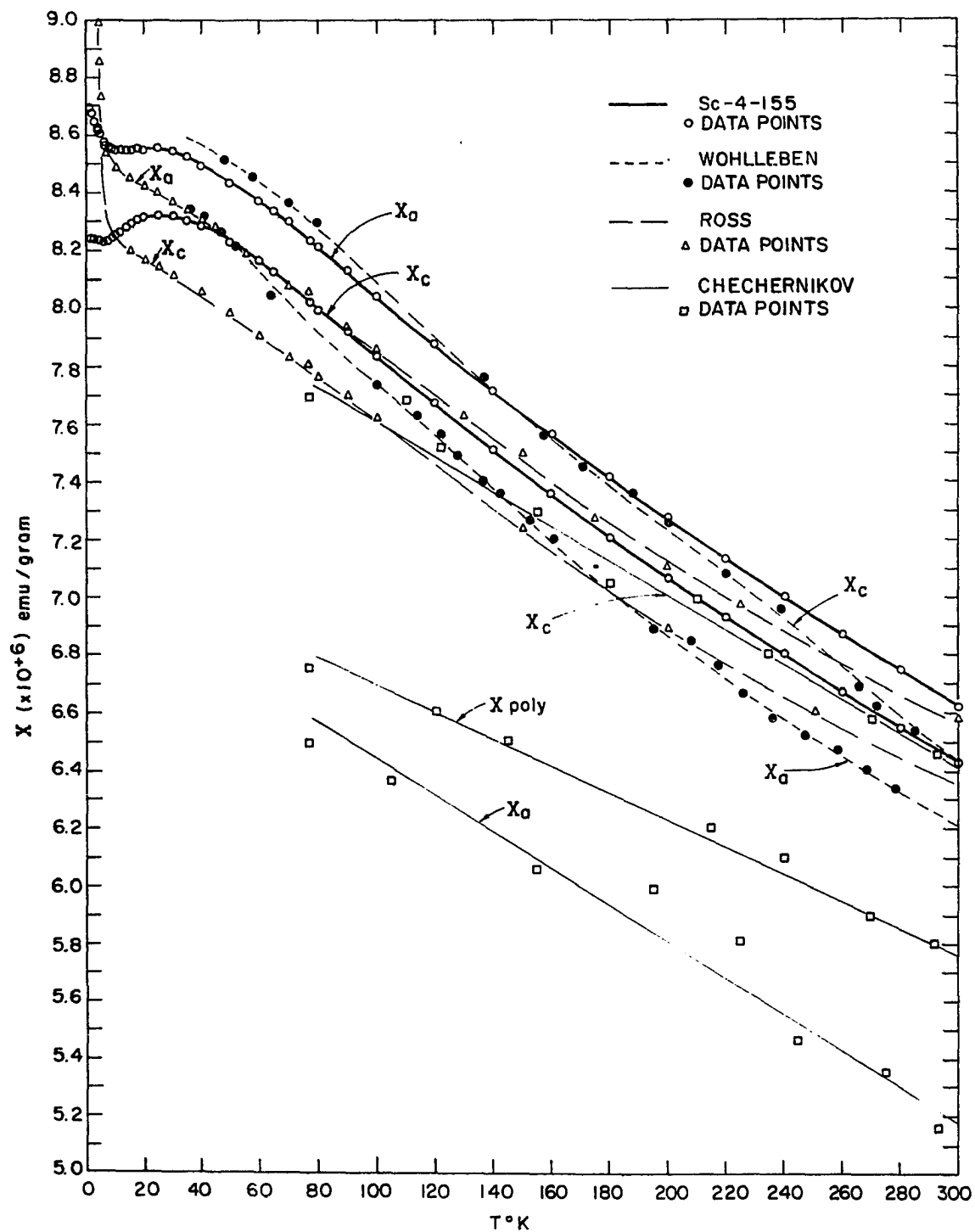


Fig. 11. Magnetic susceptibility of single crystal scandium.

in agreement with that reported by Ross et al.¹⁵ but contrary to the results of Chechernikov et al.¹¹ and Wohlleben.¹² With the exception of sample 4-160, the agreement between the various single crystals measured in this investigation was extremely good, the data differing by only .1 to .2% over the entire temperature range. The susceptibility of both the single and polycrystalline specimen prepared from metal 4-160 were approximately 1% lower than those prepared from the other two batches of metal. However as noted by the analysis in Table IV these samples contained more nonmagnetic impurities than the others, principally 900 ppm fluorine.

A plot of magnetic anisotropy vs temperature for the four single crystals is shown in Fig. 12 and shows the anisotropy to be almost linear to approximately 40°K where it rises rather sharply to a mean value of $.420 \times 10^{-6}$ emu/gram at 1.5°K. The mean room temperature anisotropy is $.192 \times 10^{-6}$ emu/gram.

Shown in Fig. 13 are plots of reciprocal susceptibility vs temperature for both single crystal axes as well as for the polycrystalline specimen. All of the data were found to exhibit Curie-Weiss behavior above approximately 70°K. From these data the Curie constants, paramagnetic Curie temperature and the effective moments of the scandium ions were calculated. These data are tabulated in Table V. For three of the crystals, 4-155-B, 4-144 and 4-160, excellent agreement was found between the calculated Curie constants for both the "a" and "c" axis.

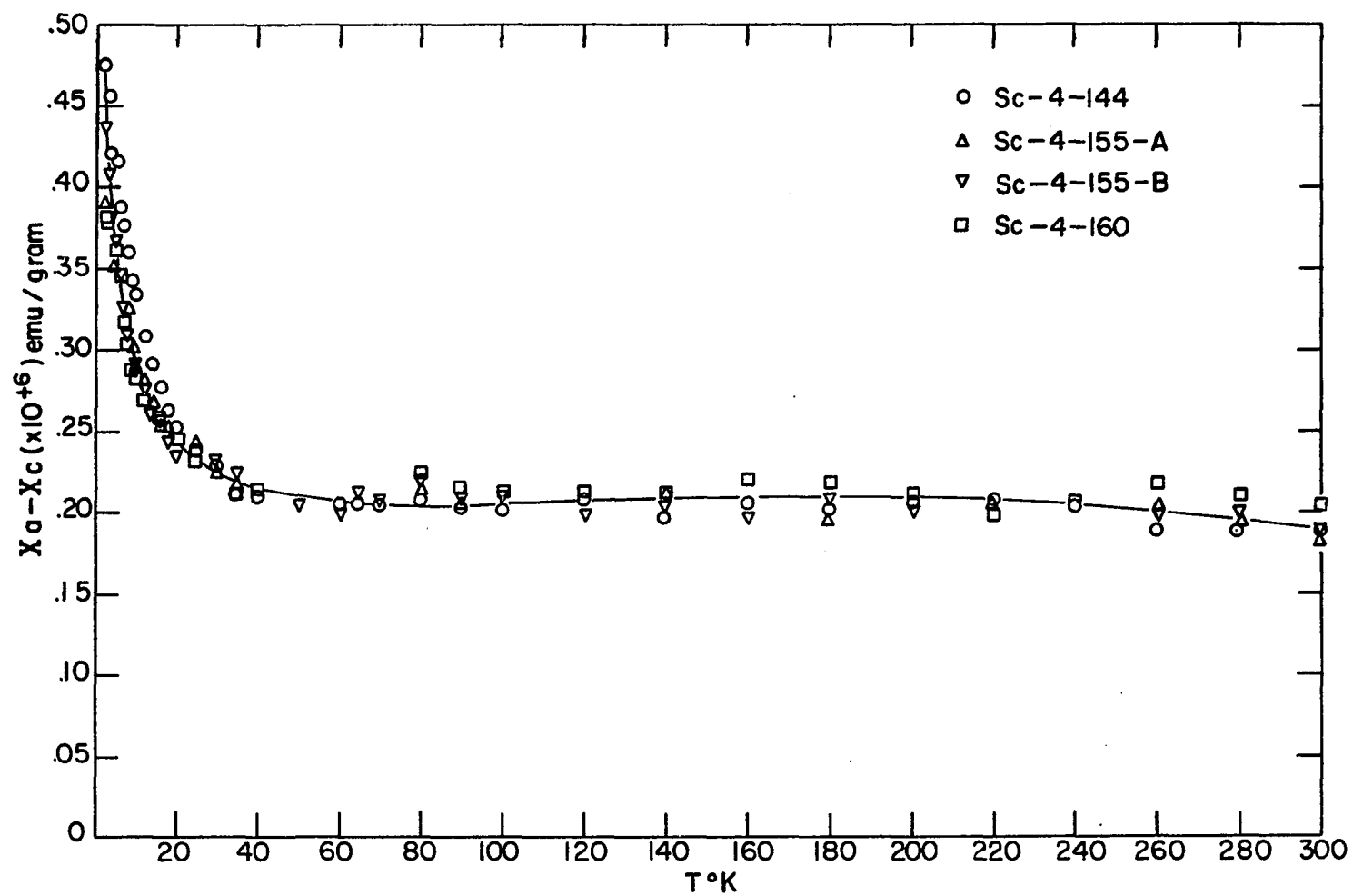


Fig. 12. Magnetic anisotropy versus temperature for single crystals of scandium.

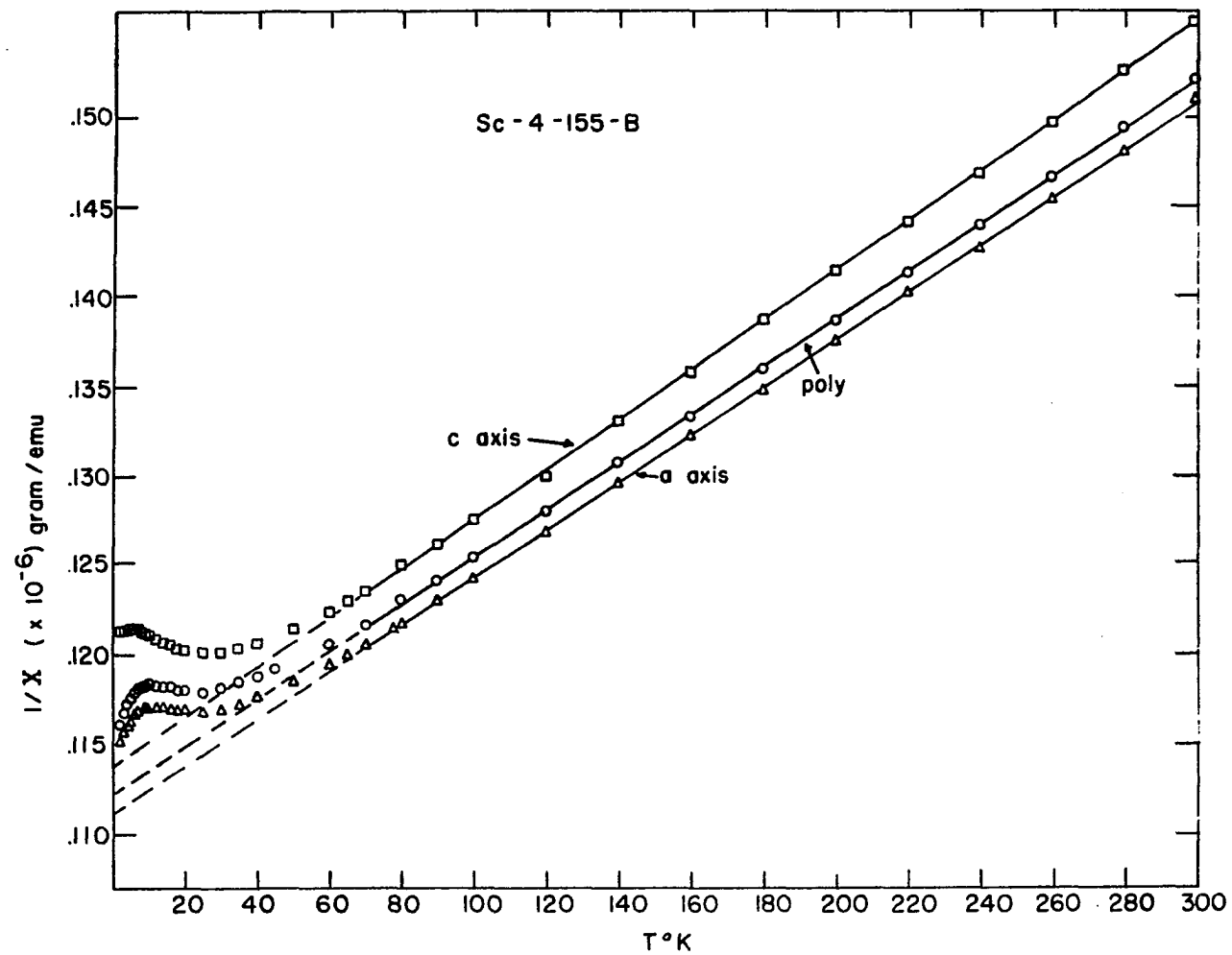


Fig. 13. Curie-Weiss plots of the susceptibility of single and polycrystalline scandium.

Table V. Curie-Weiss data for single and polycrystalline scandium.

Specimen	C^a	$\theta (^{\circ}K)$	$\mu_{eff}(\mu_B)$
4-155-B-a axis	.339	-838.7	1.64 ₆
4-155-B-c axis	.323	-816.4	1.60 ₇
4-155-A-a axis	.335	-852.5	1.65 ₉
4-155-A-c axis	.328	-831.4	1.62 ₀
4-155-poly-1	.339	-846.5	1.64 ₇
4-155-poly-2	.338	-844.2	1.64 ₅
4-155-poly-3	.340	-849.5	1.64 ₉
4-144-a axis	.338	-832.4	1.64 ₄
4-144-c axis	.322	-813.0	1.60 ₆
4-144-poly	.335	-834.5	1.63 ₆
4-160-a axis	.342	-851.8	1.65 ₂
4-160-c axis	.323	-825.8	1.60 ₈
4-160-poly	.336	-842.1	1.63 ₈

^aCurie constant/mole.

The Curie constants for both axes of crystal 4-155-A, however, were slightly higher than the average of the other three. The polycrystalline Curie constants for two of the crystals, 4-155-A and 4-160, agreed quite well with the weighted average of the single crystal values. However for crystals 4-155-B and 4-144 the polycrystalline values were slightly higher than the weighted average. This slight discrepancy may have resulted from a small amount of magnetic anisotropy such as might result from preferred orientation remaining in the polycrystalline samples or possibly from structural or impurity

effects.

3. Susceptibility of scandium alloys

The susceptibility of a number of polycrystalline scandium alloys containing known amounts of both magnetic and nonmagnetic impurities were measured from approximately 1.5 to 300°K. These impurities included hydrogen, oxygen, iron, tantalum, titanium, zirconium, hafnium, niobium, thorium, gadolinium and erbium. The samples were prepared as described in Section IV.A.4 and were all measured in the arc melted state.

It is believed that the affect of these impurities on the susceptibility would vary greatly depending on whether they form a solid solution or exist as a second phase. Whereas dissolved impurities can affect the scandium matrix itself and modify its susceptibility, any second phase would have a susceptibility of its own and add to the total susceptibility in proportion to its mole fraction. Therefore in addition to keeping the amount of solute intentionally low to minimize the possibility of saturation, all of the samples, except those doped with gadolinium and erbium, were examined metallographically to determine if any second phase was present. Gadolinium and erbium are known to form solid solutions with scandium and hence no second phase would be expected.

a. Scandium-hydrogen The susceptibility of three polycrystalline alloys containing 1.47 a/o, 1.87 a/o and 2.40 a/o hydrogen was measured from approximately 1.5 to 300°K. These data are shown in Fig. 14 along with that of the pure

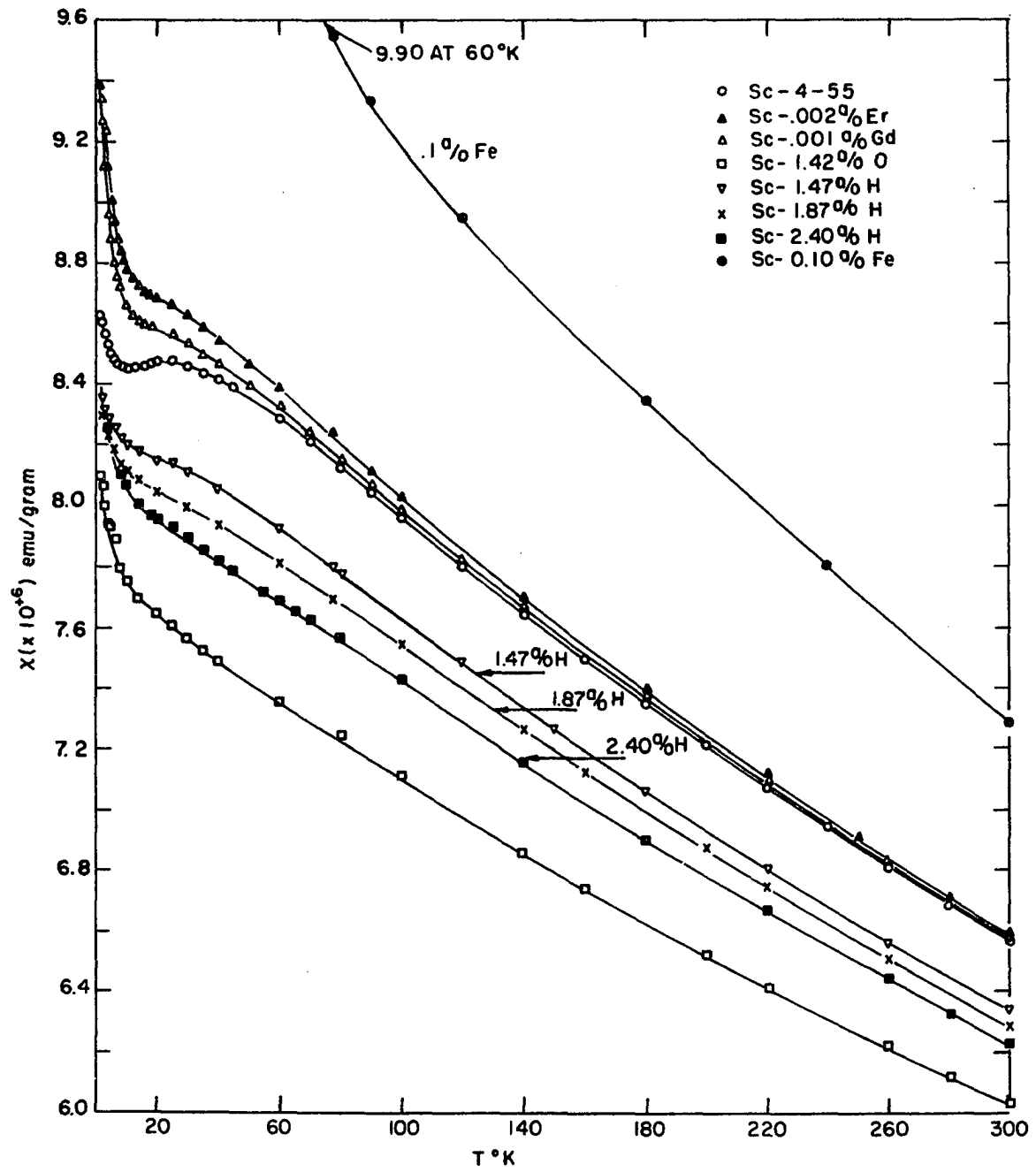


Fig. 14. The effect of a number of dilute impurities on the susceptibility of polycrystalline scandium.

scandium starting material (4-155). Listed in Table VI are the susceptibilities and the % decrease per a/o solute of the alloys at both 10 and 300°K. As noted the addition of hydrogen lowered the susceptibility almost linearly with concentration although the decrease became slightly more pronounced as the temperature was lowered. All evidence of the maximum at 30°K disappeared as the solute concentration increased. At 30°K the decrease in the susceptibility of the three alloys relative to pure scandium was found to be 2.75%, 2.91% and 2.80% per a/o solute. All of the alloys were examined metallographically and, although a very small amount of an unidentified second phase was observed in the neighborhood of the grain boundaries in the 1.87 a/o alloy, it is believed that the bulk of the hydrogen was in solution. Debye Scherrer X-ray patterns were taken and tended to confirm this, the measured lattice parameters lying well below those of hydrogen saturated scandium as determined by both Azarkh and Funin⁴⁰ and Spedding and Beaudry.³⁸

Plots of reciprocal susceptibility vs temperature were made for these alloys and all were found to exhibit Curie-Weiss behavior above 75 to 80°K. The effective moment of the scandium ion and the paramagnetic Curie temperature determined from these plots are listed in Table VI. These data show a slight increase in μ_{eff} and a quite large increase in θ with increased hydrogen concentration. The Curie-Weiss plots for the 1.47 a/o and 2.40 a/o alloys are shown in Fig. 16 along

Table VI. Decrease in the susceptibility per a/o impurity and Curie-Weiss data for scandium alloys.

Specimen	300°K		10°K		$\theta(^{\circ}\text{K})$	$\mu_{\text{eff}}(\mu_{\text{B}})$
	$\chi(\text{emu/g})$	$\Delta\chi$ (% per a/o)	$\chi(\text{emu/g})$	$\Delta\chi$ (% per a/o)		
Sc-4-155-poly	6.571		8.445		-846.5	1.647
Sc-1.47 a/o H	6.342	-2.21%	8.205	-1.93%	-876.5	1.640
Sc-1.87 a/o H	6.287	-2.31%	8.118	-2.07%	-897.6	1.647
Sc-2.40 a/o H	6.221	-2.36%	8.066	-1.87%	-897.6	1.664
Sc-0.53 a/o O	6.381	-5.32%	8.224	-4.94%	-914.0	1.641
Sc-0.71 a/o O	6.282	-6.28%	9.100	-5.75%	-947.4	1.649
Sc-1.42 a/o O	6.031	-5.79%	7.752	-5.78%	-1025.3	1.668
Sc-4-190-poly	6.611		8.639		-848.4	1.652
Sc-0.5 a/o Ti	6.550	-1.86%	8.765	+2.92%	-818.1	1.627
Sc-1.0 a/o Ti	6.533	-1.18%	8.949	+3.59%	-774.2	1.595
Sc-2.0 a/o Ti	6.451	-1.21%	9.109	+2.72%	-749.4	1.572
Sc-2.5 a/o Ti	6.460	- .91%				
Sc-3.0 a/o Ti	6.454	- .79%	9.2431	+2.33%	-727.3	1.569
Sc-3.5 a/o Ti	6.407	- .43%				
Sc-4.0 a/o Ti	6.384	- .86%	9.197	+1.61%	-714.0	1.559
Sc-5.0 a/o Ti	6.304	- .93%	9.068	+ .99%	-703.4	1.550
Sc-7.0 a/o Ti	6.171	- .95%	8.702	+ .10%	-690.1	1.540

Table VI. (Continued)

Specimen	300°K		10°K		$\theta(^{\circ}\text{K})$	$\mu_{\text{eff}}(\mu_{\text{B}})$
	$\chi(\text{emu/g})$	$\frac{\Delta\chi}{\% \text{ per a/o}}$	$\chi(\text{emu/g})$	$\frac{\Delta\chi}{\% \text{ per a/o}}$		
Sc-0.5 a/o Zr	6.535	-2.30%	8.742	-2.00%	-822.9	1.635
Sc-1.0 a/o Zr	6.452	-2.41%				
Sc-1.5 a/o Zr	6.344	-2.69%	8.598	- .31%	-817.2	1.621
Sc-0.75 a/o Hf	6.387	-4.51%				
Sc-1.0 a/o Hf	6.260	-5.32%				
Sc-1.5 a/o Hf	6.143	-4.72%	8.525	- .89%	-771.9	1.585
Sc-1.0 a/o Th	5.890	-10.91%				
Sc-1.5 a/o Th	5.547	-10.73%				
Sc-1.0 a/o Nb ^a	6.439	-2.60%				
Sc-0.1 a/o Ta	6.584	-4.05%			-840.2	1.646
Sc-0.5 a/o Ta	6.419	-5.82%	8.681	+ .97%	-800.0	1.609
Sc-1.0 a/o Ta	6.244	-5.65%			-776.1	1.586
Sc-1.5 a/o Ta	6.064	-5.52%	8.439	-1.54%	-752.0	1.560
Sc-2.0 a/o Ta	5.918	-5.24%			-753.3	1.556
Sc-3.0 a/o Ta ^a	5.840	-3.89%	7.984	-2.52%	-779.6	1.601
Sc-4.0 a/o Ta ^a	5.559	-3.98%	7.638	-2.90%	-773.3	1.583
Sc-6.0 a/o Ta ^a	5.341	-1.86%			-796.3	1.626

^aSecond phase present.

with those of several scandium-oxygen alloys.

b. Scandium-oxygen The magnetic susceptibility of three alloys containing .53 a/o, .71 a/o and 1.42 a/o oxygen are shown in Fig. 15. Listed in Table VI are the susceptibilities of these alloys at 10 and 300°K as well as the corresponding decrease per a/o solute. As with hydrogen, the addition of oxygen lowered the susceptibility, the decrease becoming more pronounced as the temperature was lowered. Likewise the % decrease was roughly linear with concentration although over twice that of hydrogen for the same amount of impurity. Other similarities included the disappearance of the maximum at 30°K. At this temperature the decrease per a/o solute was 7.86%, 8.46% and 7.44% for the .53 a/o, .71 a/o and 1.42 a/o alloys respectively. Metallographic examination of the two more dilute alloys revealed a small amount of an unidentified second phase, the bulk of which was located in the grain boundaries. Unfortunately the 1.42 a/o oxygen alloy was used as a master to prepare the two lower concentration alloys and no photomicrographs were taken. However the nominal amount of second phase in the lower concentration alloys and the reasonable linearity observed between the susceptibility and solute concentration would seem to indicate that the bulk of the oxygen was in solution.

The effective moment of the scandium ion and the paramagnetic Curie temperatures for these alloys are listed in Table VI. While only a slight increase in μ_{eff} was observed,

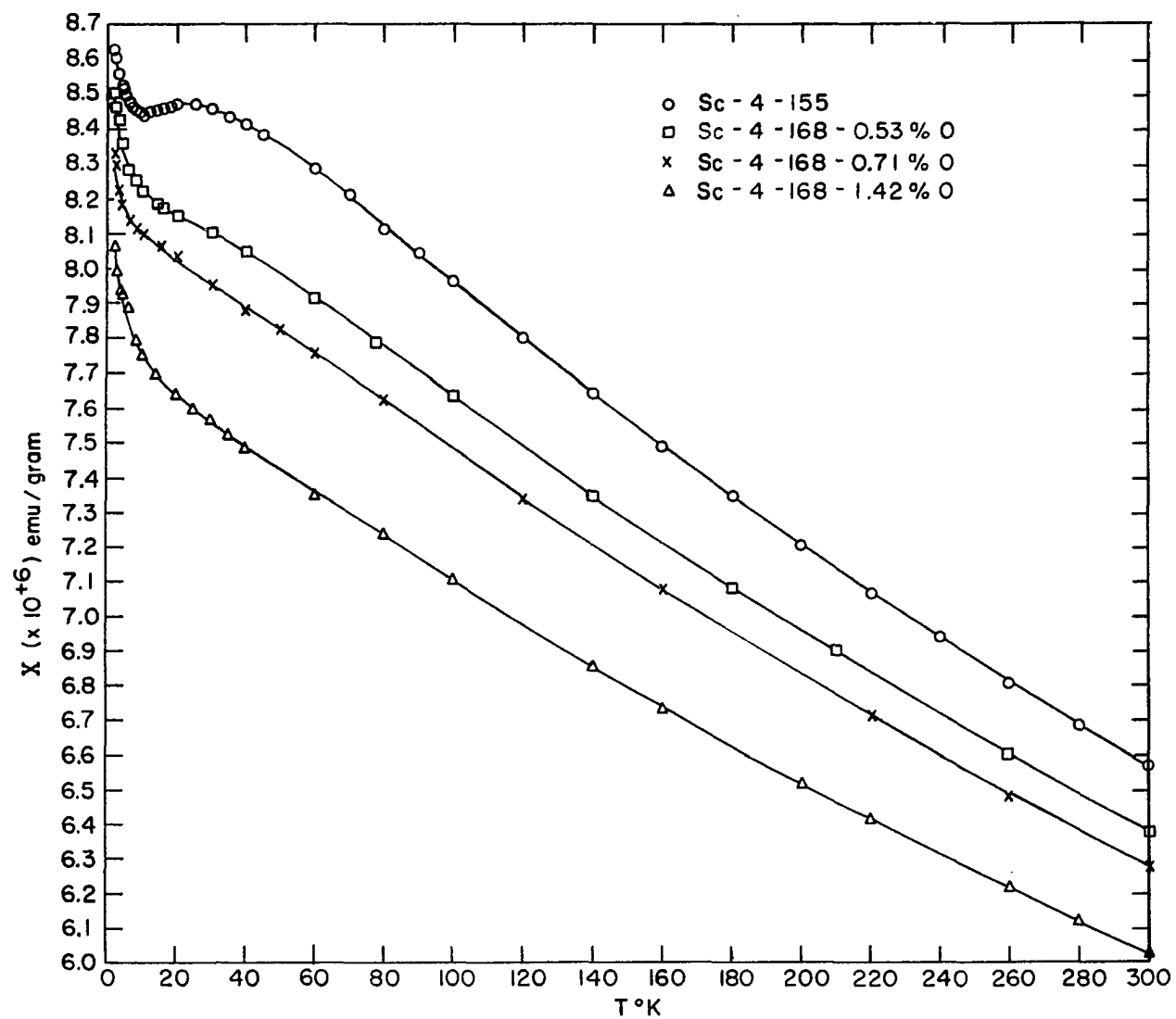


Fig. 15. Effect of oxygen on the magnetic susceptibility of polycrystalline scandium.

θ was found to increase considerably with increased solute concentration. The .53 a/o, .71 a/o and 1.42 a/o alloys were found to exhibit Curie-Weiss behavior to 70, 50 and 25°K respectively. Curie-Weiss plots for the .53 a/o and 1.42 a/o alloys are shown in Fig. 16.

c. Scandium-iron A scandium-0.1 a/o iron alloy was measured from 60 to 300°K and its susceptibility for a field strength of 11,555 gauss is shown in Fig. 14. In contrast to Wohllleben¹² who found that the addition of iron lowered the susceptibility of scandium, an increase was observed in this arc melted sample. The sample exhibited considerable field dependence even at high temperatures. At 77 and 300°K field dependent moments of .0134 and .0066 emu/gram were found respectively. Metallographic examination revealed second phase precipitates located primarily at the grain boundaries. This observation together with the field dependence suggests that due to its limited solubility, at least part of the iron precipitates to form iron rich clusters, probably intermetallic compounds, which are large enough to go ferromagnetic at room temperature. It seems reasonable that as the temperature of the sample is lowered smaller clusters, which formerly behaved paramagnetically due to thermal agitation, become ferromagnetic, increasing the field dependence of the sample.

d. Scandium-tantalum The susceptibilities of a series of scandium-tantalum alloys ranging in concentration from 0.1 to 6.0 a/o are shown in Fig. 17. Also shown is the

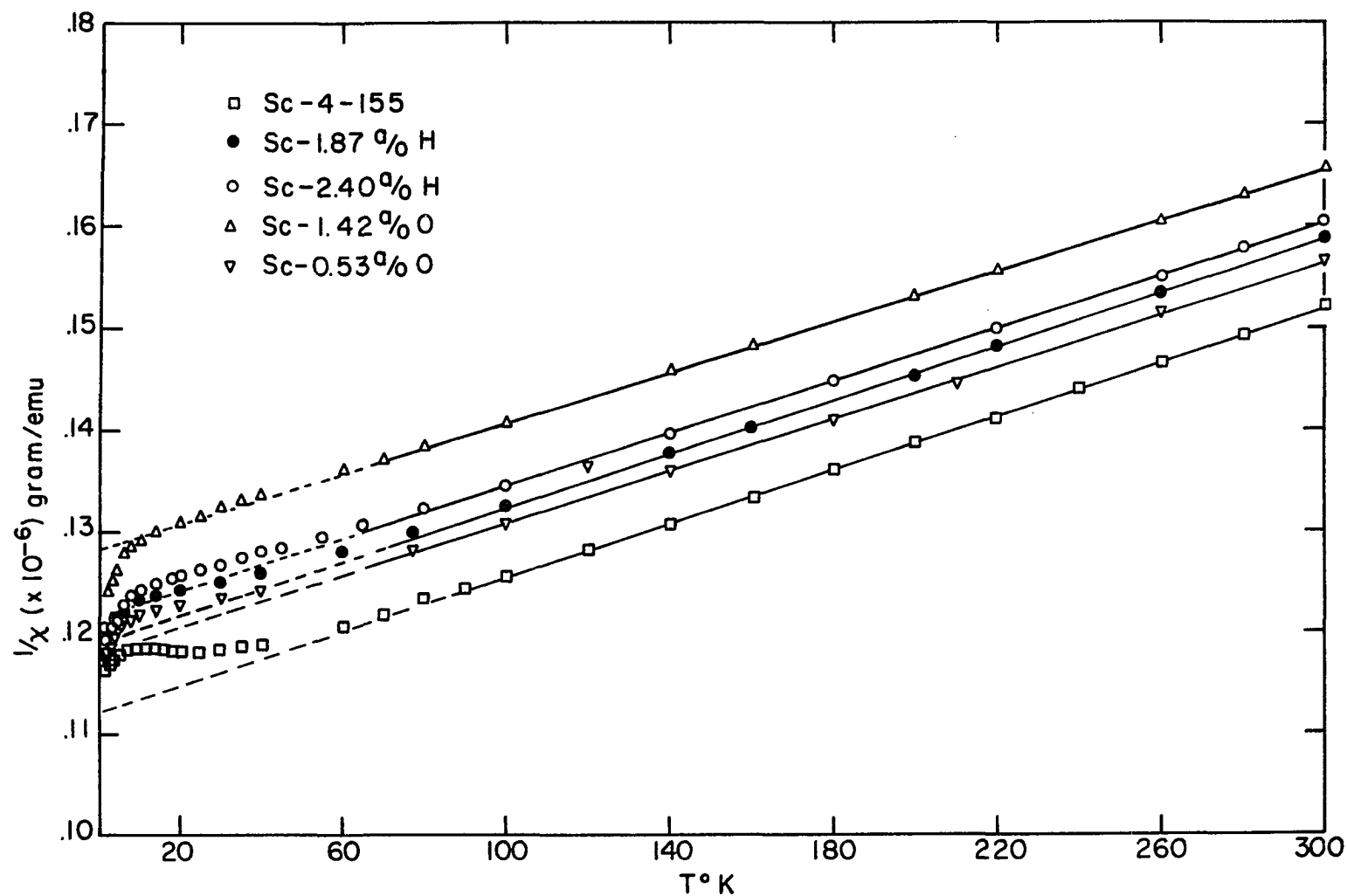


Fig. 16. Plots of reciprocal susceptibility versus temperature for pure polycrystalline scandium and several scandium-hydrogen and scandium-oxygen alloys.

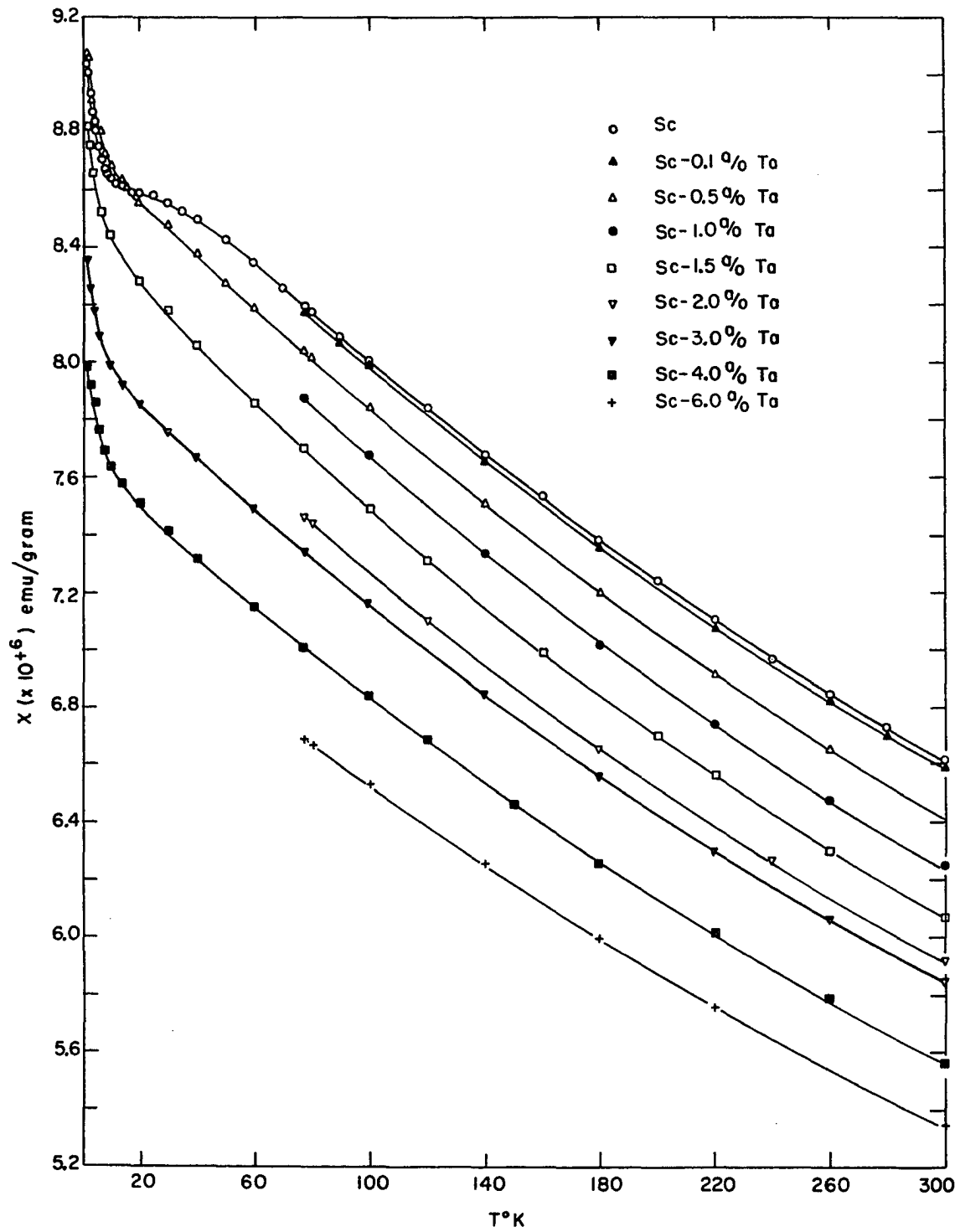


Fig. 17. The effect of tantalum on the magnetic susceptibility of polycrystalline scandium.

susceptibility of polycrystalline Sc-4-190, the metal from which the alloys were prepared. All of the alloys were found to have a lower susceptibility than pure scandium and the maximum at 30°K was no longer observed. This lowering was fairly linear with decreasing temperature to approximately 60°K. At lower temperatures the decrease was found to be somewhat less and, for the more dilute alloys, actually higher than pure scandium. Listed in Table VI are the susceptibility values as well as the % decrease per a/o tantalum at both 300° and, where available, 10°K. These room temperature data are plotted as a function of both a/o and w/o tantalum in Fig. 18. Also plotted is the straight line relationship between the room temperature susceptibility of the scandium starting material (6.611×10^{-6} emu/gram) and the room temperature susceptibility of tantalum ($.850 \times 10^{-6}$ emu/gram). This line would represent the susceptibility of the alloys if the two components were completely inhomogeneous in which case the tantalum would add to the total susceptibility in proportion to its mole fraction only. As noted the susceptibility decreases fairly linearly up to 2 a/o tantalum but at 3 a/o tantalum a bump was observed. A second alloy of this concentration was prepared and almost identical results were found. The significance of this bump is in doubt because a considerable amount of second phase was found in this sample. However it must be noted that a similar bump was found at 3 a/o

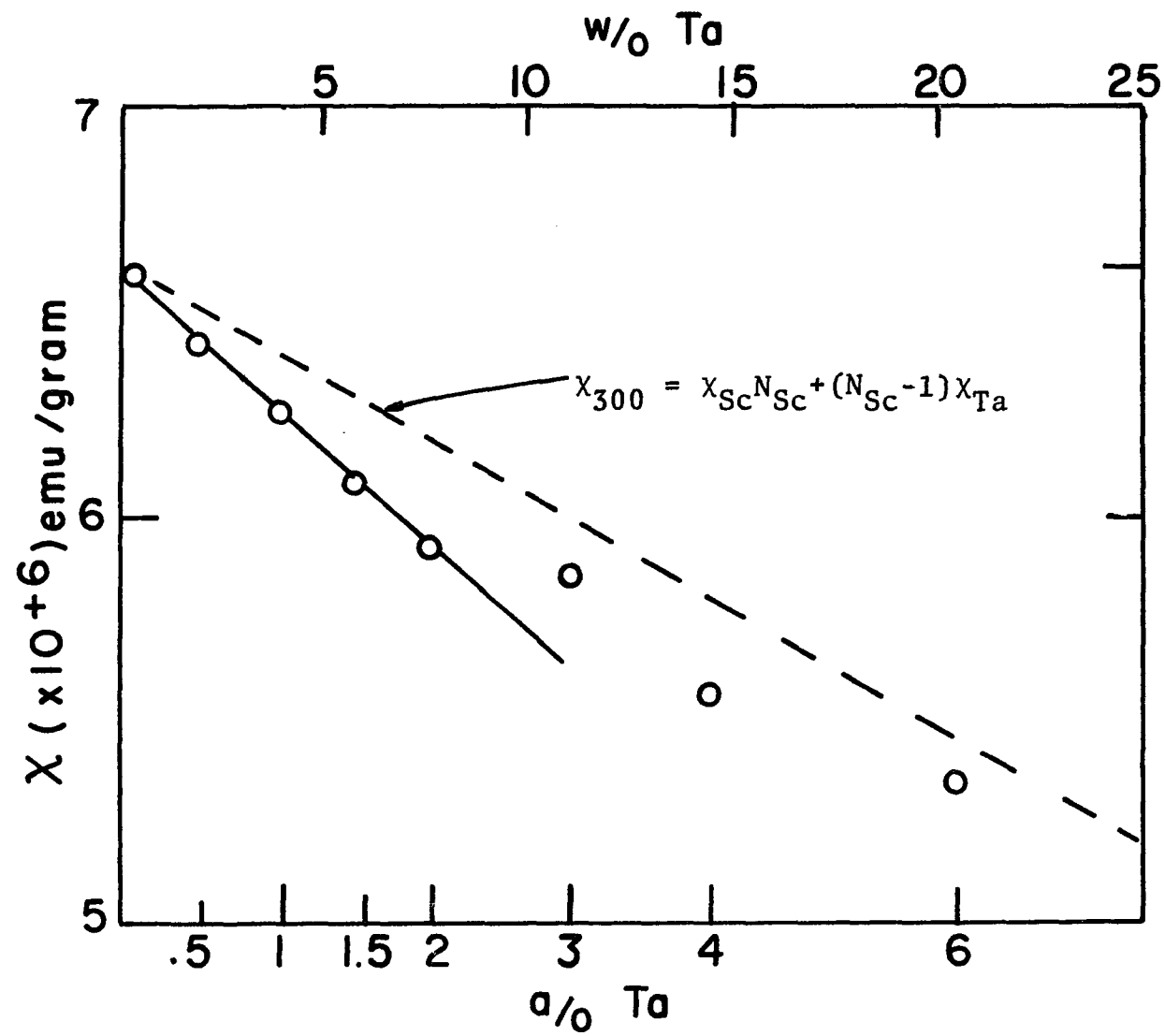


Fig. 18. Susceptibility of a series of scandium-tantalum alloys at 300°K.

in a series of scandium-titanium alloys. The values above 3 a/o were again lower but definitely appeared to approach the dashed line representing a completely inhomogeneous solution. This trend was seen as indicating that the solubility limit had been exceeded. Metallographic examination confirmed this, the alloys above 2 a/o showing considerable second phase while the less concentrated alloys did not. Debye Scherrer X-ray patterns also revealed a steady decrease in both the "a" and "c" axis parameters up to and including the 2 a/o tantalum. This agrees with Dennison et al.⁴¹ who found that the solubility of tantalum at the melting point of scandium is 3.2 a/o. At room temperature this value would be somewhat lower since in an arc melted sample all of the dissolved tantalum would not be quenched into solution.

The Curie-Weiss data calculated from plots of reciprocal susceptibility vs temperature are tabulated in Table VI. The effective moment of the scandium ion was found to decrease with increasing solute concentration up to 2 a/o tantalum. Above 2 a/o μ_{eff} was found to increase. The values for θ behaved similarly, decreasing to 2 a/o and then increasing. This is in sharp contrast to the hydrogen and oxygen alloys where a steady increase with increased solute concentration was observed. However for these alloys the solubility limit was not believed to have been exceeded as was the case for tantalum. Shown in Fig. 19 are the Curie-Weiss plots for the pure scandium starting material as well as the 0.5 a/o, 1.5

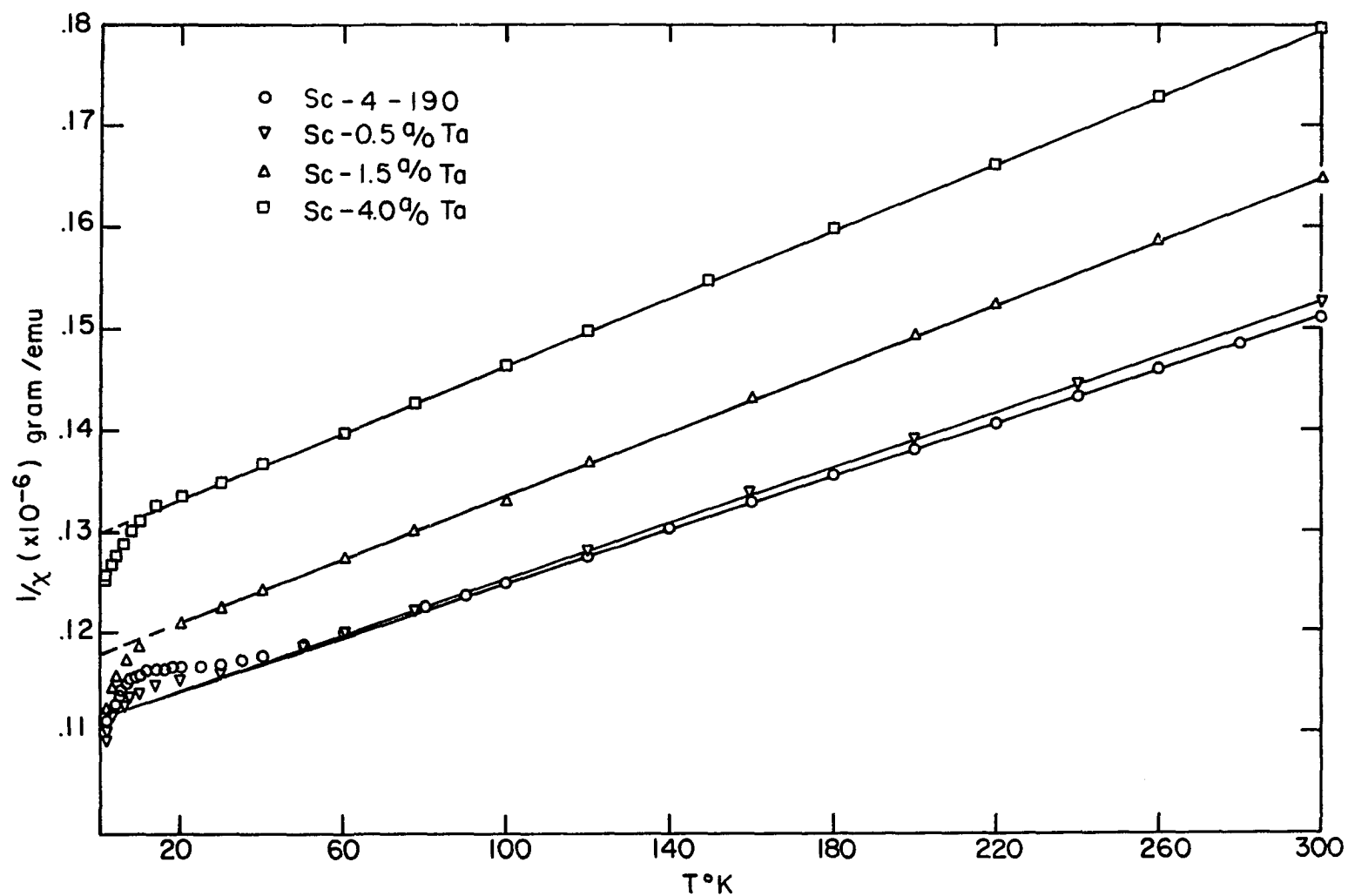


Fig. 19. Plots of reciprocal susceptibility versus temperature for pure scandium and several scandium-tantalum alloys.

a/o and 4.0 a/o alloys. As noted, the temperature above which Curie-Weiss behavior was found decreased with increasing tantalum concentration.

The scandium used to make the tantalum alloys was not as pure as that used in making the oxygen and hydrogen alloys. This metal, 4-190, did contain slightly more rare earth impurities and this is reflected in the slightly sharper upturn in the data at low temperatures. This metal had a field dependent moment of .0025 emu/gram at 1.63°K which would correspond to 9.3 ppm of saturated gadolinium if this were the only impurity present. In addition the maximum observed at 30°K in the purer scandium was no longer evident. Its analysis in ppm atomic is as follows: H, 758; C, 30; N, 10; O, 343; F, 30; Fe, 16; Ce, 2.2; Pr, .6; Nd, .5; Sm, .3; Eu, <.2; Gd, 2.4; Tb, .5; Dy, 1.1; Ho, 6; Er, 1.2; Tm, <.2; Yb, <.5 and Ta, 100.

e. Scandium-titanium The susceptibility of a series of scandium-titanium alloys ranging in concentration from 0.5 a/o to 7.0 a/o titanium was measured. Without exception the susceptibilities of these alloys were lower and higher than that of scandium at high and low temperatures respectively. Shown in Fig. 20 is the temperature dependence of the susceptibility of the .5 a/o, 1 a/o, 3 a/o and 5 a/o alloys. To avoid confusion all of the data are not shown. The 2.5 a/o and 3.5 a/o alloys were measured at room temperature only. Also shown in Fig. 20 are plots of susceptibility vs w/o and a/o

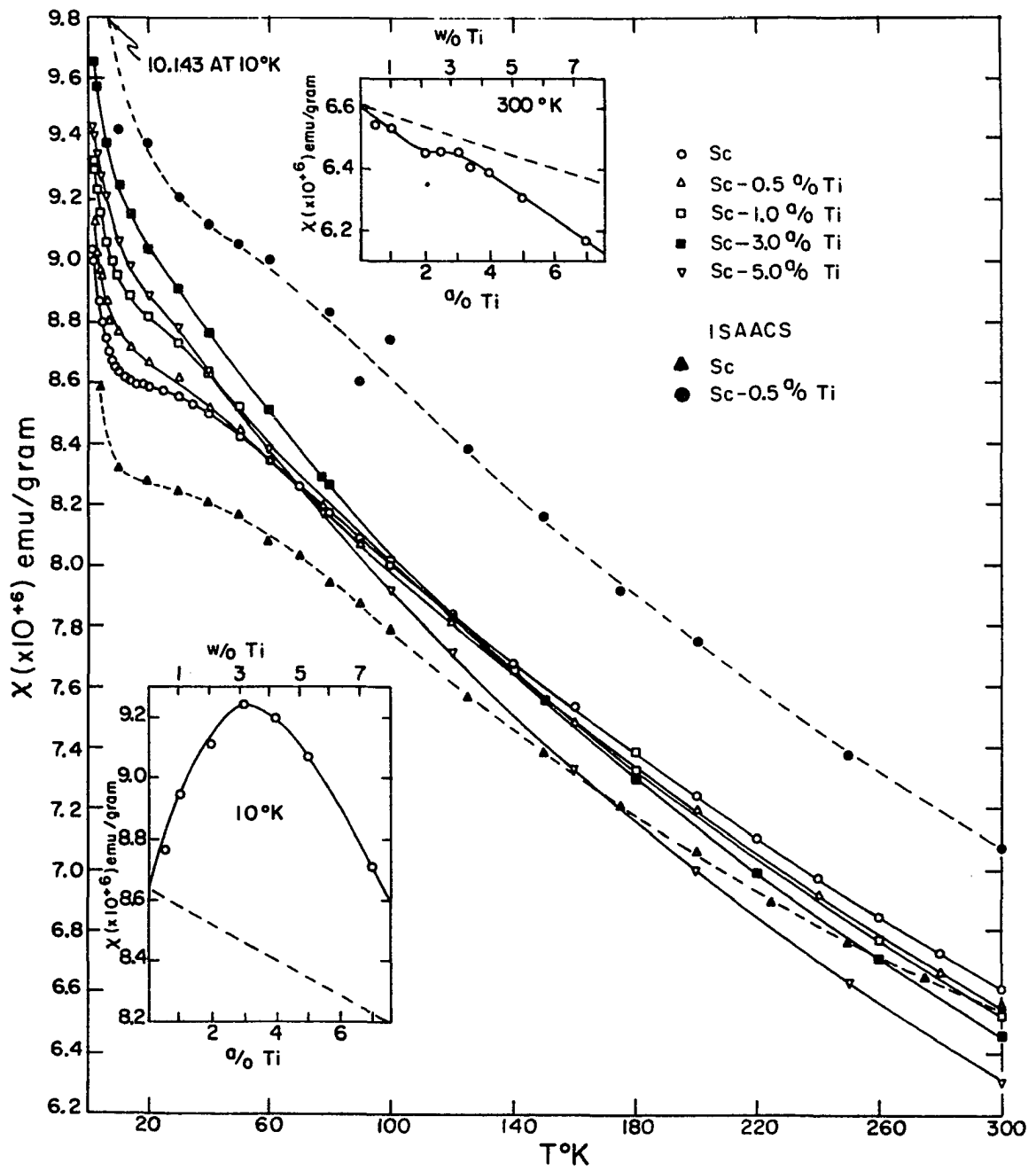


Fig. 20. The effect of titanium on the magnetic susceptibility of polycrystalline scandium.

titanium at both 300 and 10°K. Both curves indicate anomalous behavior at approximately 3 a/o titanium. At low temperatures the susceptibility first increases and, then beyond 3 a/o, decreases with increased solute concentration. At high temperature the decrease in the susceptibility was found to be almost linear with concentration up to 2 a/o solute. Above this concentration the susceptibility increased slightly and then again decreased. The dashed line in these plots represents the straight line relationship between the susceptibility of pure scandium and that of titanium at the same temperature and would represent the susceptibility of the alloy if the two components were completely inhomogeneous. Values used for the susceptibility of titanium at 300°K and 10°K were 3.36 and 3.06×10^{-6} emu/gram respectively.⁷ All of the alloys were examined metallographically and none were found to contain any second phase precipitates. Likewise Debye Scherrer X-ray patterns revealed a linear decrease in both the "a" and "c" axis parameters with increased solute concentration, indicating that a solid solution had been formed. This agrees with the results of the scandium-titanium system by Beaudry and Daane⁴² who found the maximum solubility of titanium in scandium to be 13.5 w/o.

All of the alloys were found to exhibit Curie-Weiss behavior although the temperature to which such behavior was observed varied considerably with concentration. Curie-Weiss plots for the 0.5 a/o, 1 a/o and 5 a/o alloys are shown in

Fig. 21 and show that the Curie-Weiss law is obeyed to 50°K, 10°K and 160°K for the three alloys respectively. All but the 0.5 a/o alloy, showed negative deviation from Curie Weiss behavior at low temperature. The fact that the 1 a/o alloy obeys the Curie-Weiss relationship to such low temperatures is not thought to be significant, reflecting only the transition between positive and negative deviation found in these alloys. The Curie-Weiss data for these alloys are tabulated in Table VI. A slight decrease in the effective moment of the scandium ion and a fairly large decrease in the paramagnetic Curie temperature was found with increased solute concentration.

The titanium used to make these alloys was completely analyzed and, with the exception of 107 ppm (atomic) iron, no major impurities were found. Due to the fairly dilute nature of the alloys this amount of iron would have only a slight effect on the susceptibility, and then only at low temperatures. No field dependence was found in any of these alloys above liquid helium temperature.

Also shown in Fig. 20 are the data for scandium and a scandium-0.5 a/o titanium alloy measured by Isaacs et al.¹⁶ Contrary to the results of this study, they found that titanium in this concentration increased the susceptibility of scandium by a considerable amount at all temperatures. The cause of this discrepancy is not known.

f. Scandium-Zr, Hf, Nb, Th The susceptibility of three alloys containing 0.5 a/o, 1.0 a/o and 1.5 a/o zirconium

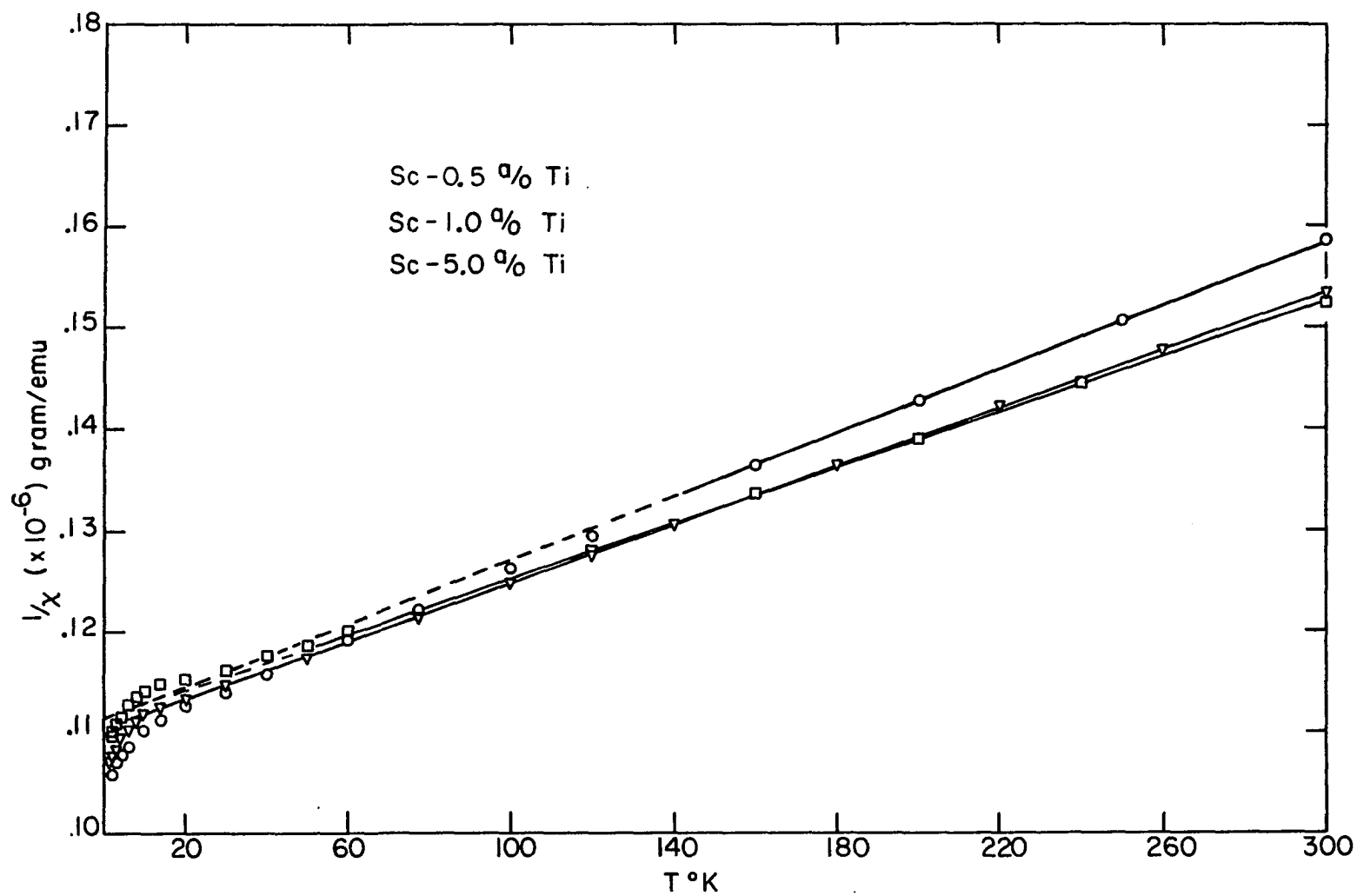


Fig. 21. Plots of reciprocal susceptibility versus temperature for several scandium-titanium alloys.

was measured. The temperature dependence of the susceptibility of the 0.5 a/o and 1.5 a/o alloys is shown in Fig. 22. The 1.0 a/o alloy was measured at room temperature only. The effect of zirconium on the susceptibility of scandium was found to be somewhat similar to that caused by titanium. At 300°K the susceptibility decreased almost linearly with solute concentration. At low temperature the susceptibility was initially greater than pure scandium but for the 1.5 a/o alloy was slightly less. Both the susceptibility and the change in the susceptibility at 300 and 10°K for these alloys are listed in Table VI. Also listed are the Curie-Weiss data for the 0.5 a/o and 1.5 a/o alloys. As with the scandium-titanium alloys, both the effective moment of the scandium ion and the paramagnetic Curie temperature decreased with increased solute concentration. The 0.5 a/o and 1.5 a/o alloys were found to exhibit Curie-Weiss behavior to 50 and 10°K respectively.

Three alloys containing 0.75 a/o, 1.0 a/o and 1.5 a/o hafnium were also measured. The 1.5 a/o alloy was measured from approximately 1.6 to 300°K and the susceptibility is shown in Fig. 22 along with the scandium-zirconium alloys. A clear trend is seen in proceeding from titanium to zirconium to hafnium. In all cases the high temperature susceptibility is lower while the low temperature data is either higher or only slightly lower. As noted in Table VI both the effective moment of the scandium ion and the paramagnetic Curie temperature are lower than that of pure scandium metal. All three of

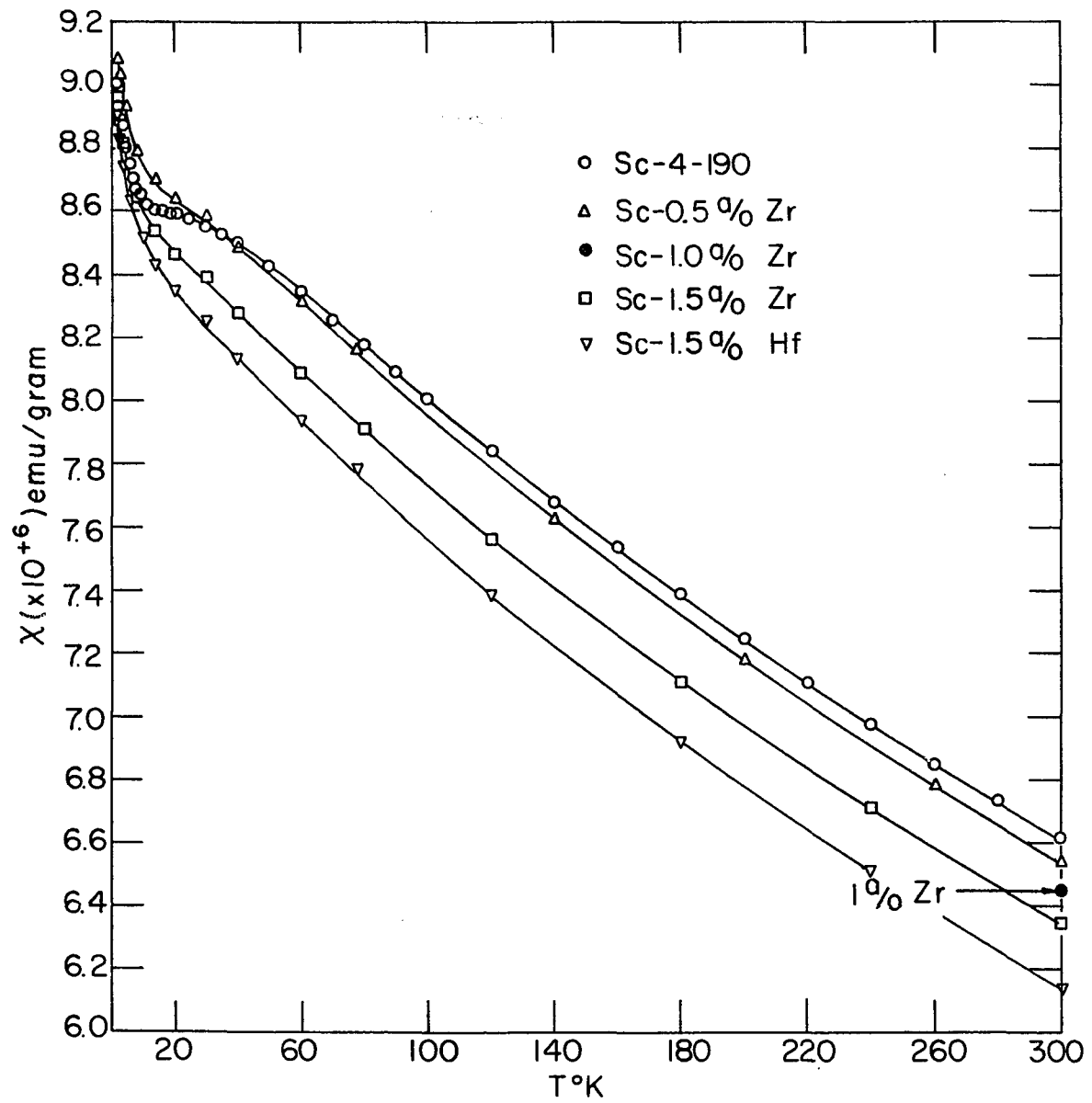


Fig. 22. The effect of zirconium and hafnium on the magnetic susceptibility of polycrystalline scandium.

these alloys as well as the scandium-zirconium alloys were examined metallographically and all were free of second phase except the 1.5 a/o hafnium alloy. This sample had a very small amount of an unidentified second phase in the grain boundaries.

Alloys containing 1.0 a/o niobium and 1.0 a/o and 1.5 a/o thorium were also measured at room temperature. All of these alloys were found to have a lower susceptibility than that of pure scandium. Tabulated in Table VI are their respective susceptibilities at room temperature and the % decrease relative to pure scandium. All were examined metallographically and considerable second phase was observed.

d. Scandium-gadolinium A number of scandium alloys containing .001 a/o, .01 a/o, .05 a/o, .1 a/o and 1 a/o gadolinium were measured from approximately 1.6°K to 300°K. Plots of susceptibility vs temperature for the latter four alloys are shown along with that of pure scandium in Fig. 23. For reasons of clarity the susceptibility of the .001 a/o alloy is shown in Fig. 14. The field dependence of all of these alloys was measured and none was observed above 9°K for even the most concentrated alloys.

The contribution of the solute atoms to the susceptibility was determined by subtracting off the susceptibility of the pure metal. The effective moment of the gadolinium ion was then determined from plots of $1/\chi$ vs temperature. Several of these plots, including those for the .001 a/o, and 1 a/o

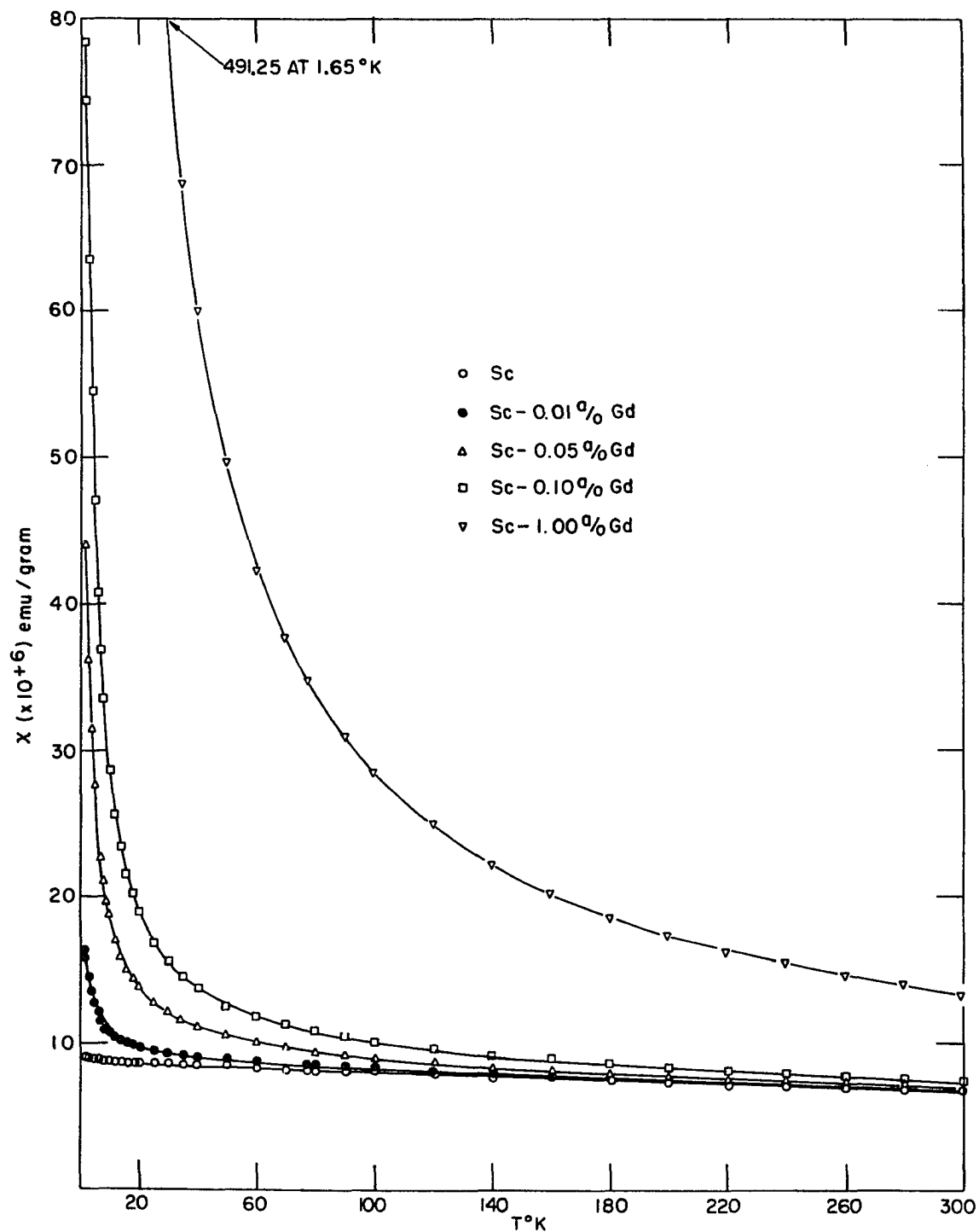


Fig. 23. Magnetic susceptibility of a series of polycrystalline scandium-gadolinium alloys.

alloys, are shown in Figs. 24 and 25. For the 1 a/o and 0.1 a/o alloys little scatter or deviation from Curie Weiss behavior was observed in this data at higher temperatures. The amount of scatter increased with decreasing solute concentration and was especially evident in the .001 a/o alloy above approximately 30°K. This is because the difference in the susceptibility between the alloys and that of pure scandium is only slightly greater than the experimental accuracy of the measurements. Below approximately 6°K a slight deviation from Curie-Weiss behavior was observed in the .01 a/o to 1.0 a/o alloys. This deviation occurred at approximately 8°K in the .001 a/o alloy. For this reason the effective moments were calculated between 6 and 60°K for the more concentrated alloys and between 8 and 30°K for the most dilute alloy.

The effective moments of the gadolinium ion determined from the susceptibility of these alloys are tabulated in Table VII along with their corresponding paramagnetic Curie temperatures. The effective moments were found to be independent of solute concentration, averaging roughly $8.80 \mu_B$. This is roughly 10% larger than the free ion value of $7.98 \mu_B$. To determine the reliability of these data two additional alloys containing .01 a/o and 0.1 a/o gadolinium were measured. From these results the experimental error is believed to be approximately $\pm .1 \mu_B$ for the most concentrated to $\pm .2 \mu_B$ for the most dilute alloys.

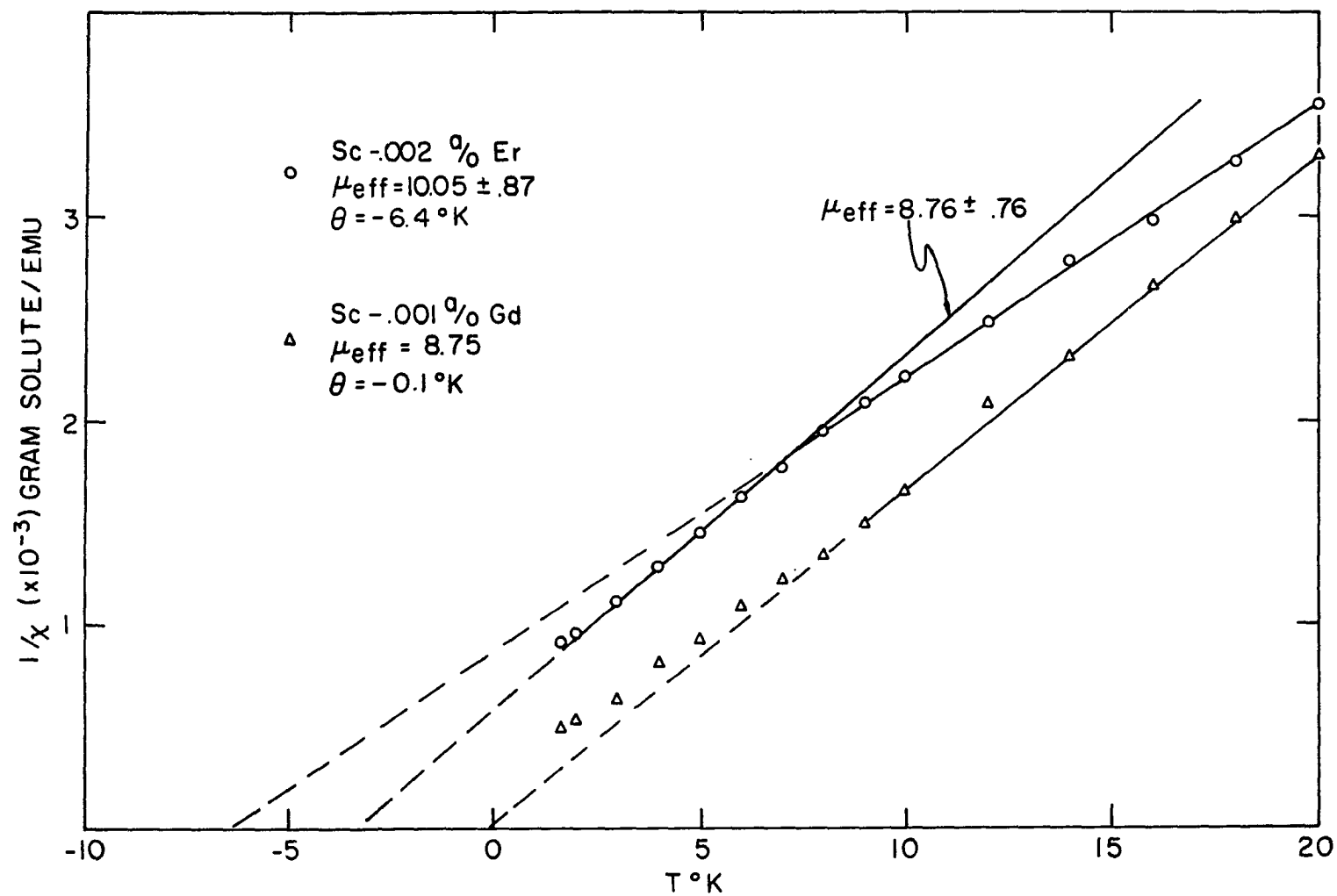


Fig. 24. Curie-Weiss plots of the susceptibility of .001 a/o gadolinium and .002 a/o erbium in scandium.

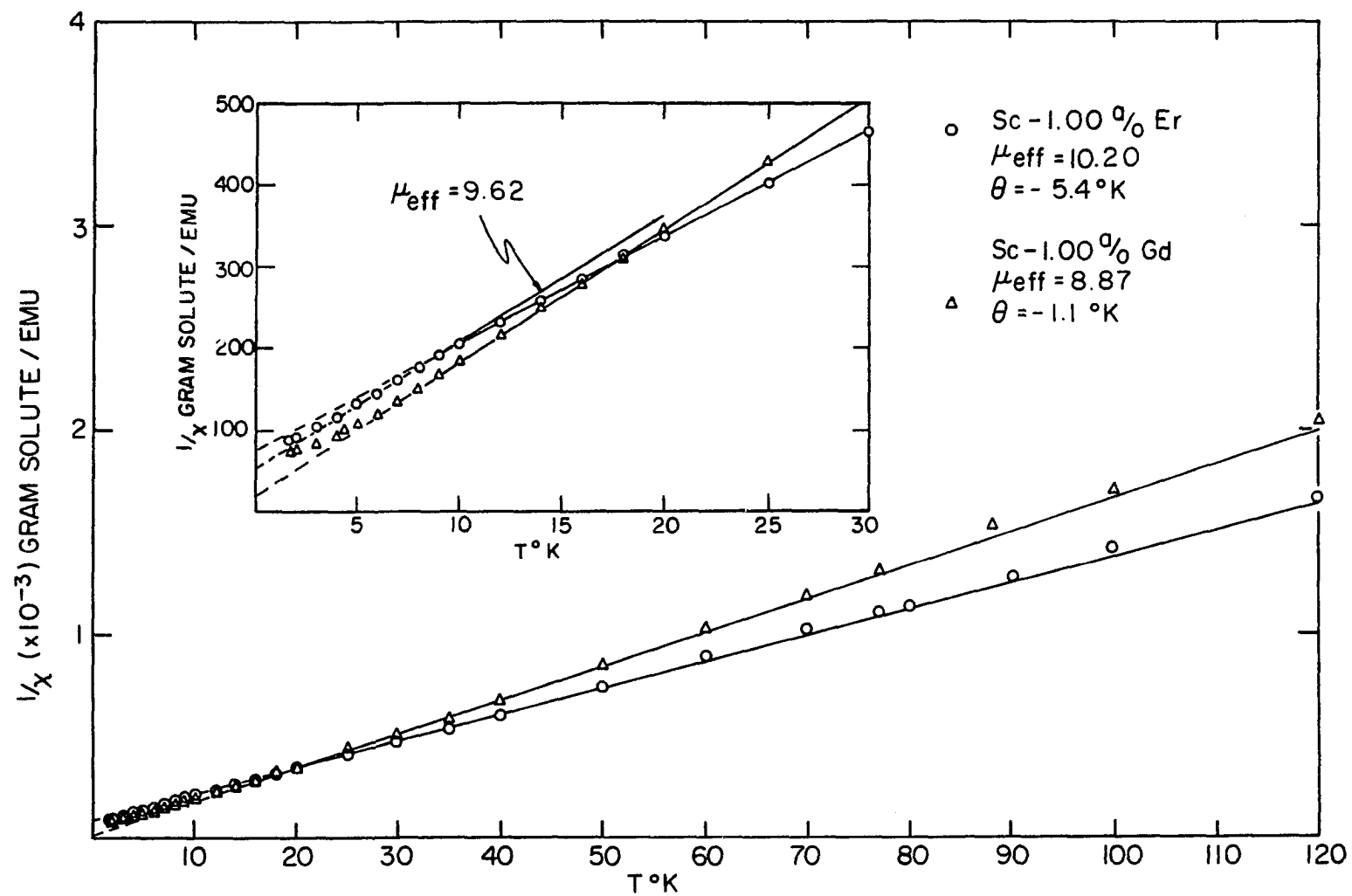


Fig. 25. Curie-Weiss plots of the susceptibility of 1 a/o gadolinium and erbium in scandium.

Table VII. Dependence of the effective moment of gadolinium atom and paramagnetic Curie temperature on gadolinium concentration.

Gd conc. (a/o)	No. 1		No. 2	
	$\mu_{\text{eff}}(\mu_B)$	$\theta(^{\circ}\text{K})$	$\mu_{\text{eff}}(\mu_B)$	$\theta(^{\circ}\text{K})$
.001	8.75	-0.10		
.01	8.64	-0.26	8.89	-0.63
.05	8.72	-0.52		
.10	8.81	-0.65	8.88	-0.65
1.00	8.87	-1.13		

e. Scandium-erbium A number of scandium alloys containing dilute amounts of erbium were also measured. Initially a sample determined by mass spectrograph analysis to contain 20 ppm erbium was measured. The susceptibility of this sample is shown in Fig. 14. The erbium in this sample was found to obey a Curie-Weiss law with an effective moment of $9.98 \pm .78 \mu_B$ and a paramagnetic Curie-Weiss temperature of -6.6°K , the range of values resulting from the $\pm 20\%$ accuracy of the mass spectrograph analysis. The plot of reciprocal susceptibility vs temperature is shown in Fig. 24 along with a similar curve for a scandium-.001 a/o gadolinium alloy. It is observed that below 8°K the data deviates from Curie-Weiss behavior. The effective moment and paramagnetic Curie-Weiss temperature from these low temperature data was $8.76 \pm .76 \mu_B$ and -3.4°K respectively.

To better understand the behavior of these dilute impurities three additional alloys containing .01 a/o, .1 a/o and

1 a/o erbium were prepared. The temperature dependence of the susceptibility of these alloys are shown in Fig. 26 along with that of pure scandium. The effective moments of these alloys are tabulated in Table VIII along with their corresponding paramagnetic Curie-Weiss temperatures. The moments were found to be fairly constant with erbium concentration, averaging around $10.08 \mu_B$.

Due to the scatter in the data at higher temperatures the effective moments were calculated from 10 to 50°K for the most concentrated and between 10 and 30°K for the most dilute alloys.

At low temperatures, i.e. below 10°K , all of the alloys showed deviation from Curie-Weiss behavior. The effective moments calculated from these low temperature data are all lower than the high temperature values. These moments are also listed in Table VIII.

Table VIII. Dependence of the effective moment of erbium atom and paramagnetic Curie-Weiss temperature on erbium concentration.

Er conc. (a/o)	High temp, $> 15^\circ\text{K}$		Low temp, $< 10^\circ\text{K}$	
	$\mu_{\text{eff}}(\mu_B)$	$\theta(^{\circ}\text{K})$	$\mu_{\text{eff}}(\mu_B)$	$\theta(^{\circ}\text{K})$
.002+20%	$10.05 \pm .87$	-6.4	$8.76 \pm .76$	-3.4
.01	10.13	-5.6	9.31	-3.3
.10	9.97	-6.9	8.46	-3.0
1.00	10.20	-5.4	9.62	-4.1

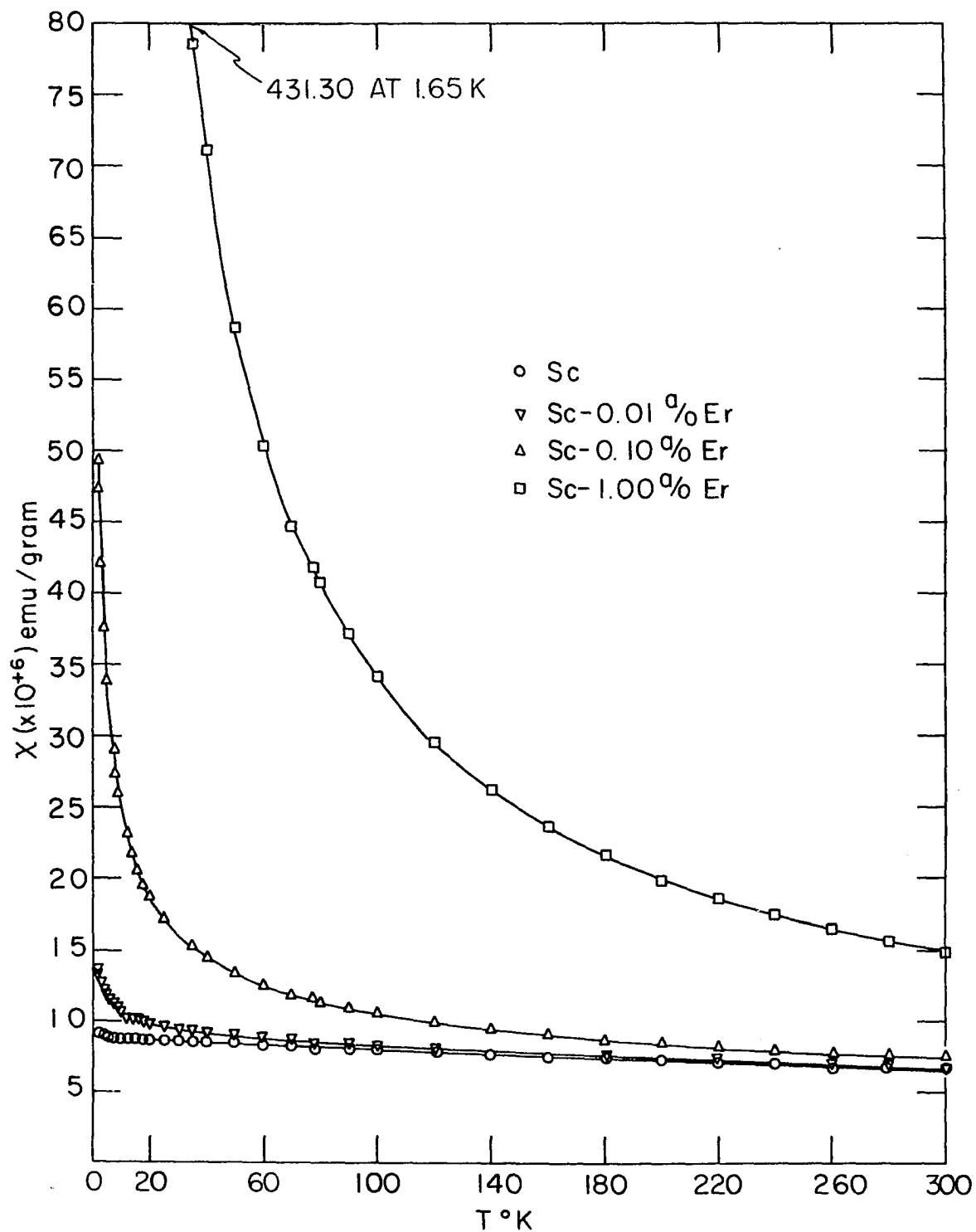


Fig. 26. Magnetic susceptibility of a series of polycrystalline scandium-erbium alloys.

B. Yttrium

1. Sample purity

Four single crystals, designated 4-84, 4-85-A, 4-85-B and 4-170, were prepared from three separate batches of metal. Crystals 4-85-A and B were prepared separately from the same batch and, due to the similarity of their susceptibility, only one was given a thorough analysis. The analyses of these crystals are shown in Table IX. Any impurity not listed was present in a concentration of less than 1 ppm atomic.

All of the samples were also measured for a field dependence at low temperatures to determine their relative purity. At the lowest temperatures, all of these specimens had more field dependence than the purest scandium samples but none exhibited any above 5°K. The intercepts of plots of moment vs magnetic field, which represents the field dependent moment, were .00069, .00132 and .00211 emu/gram for metals 4-84, 4-85 and 4-170 respectively. This would correspond to 2.6 ppm, 4.9 ppm and 7.9 ppm of saturated gadolinium if this were the only impurity present.

2. Susceptibility of pure yttrium

The temperature dependence of the susceptibility of the purest yttrium sample, 4-84, is shown in Fig. 27 along with the results of several previous investigations by Chechernikov *et al.*²³ and Gardner and Penfold.²¹ These same data are shown in Fig. 41 along with that found in this investigation for

Table IX. Analyses of yttrium metal in ppm atomic

Element	4-84	4-85	4-170	Element	4-84	4-85	4-170
H	167(1.9) ^a	1778(20)	520(5.9)	Cu	10	9	≤.1
C	140(19)	222(30)	200(27)	Sc	3	30	≤.2
N	57(9)	25(4)	749(118)	La	1.5	1.3	1
O	750(135)	966(174)	644(116)	Ce	.5	.4	1.5
F	7(1.4)	234(50)	<3(<3)	Pr	.8	1.1	.2
Na	7	2	N.D.	Nd	<.6	<.6	<.3
Mg	5	1	.06	Sm	<.4	<.4	<.2
Al	3	4	≤3	Eu	<.2	<.2	<.01
Si	<3	<3	2	Gd	5.3	7	3
Cl	16	40	1	Tb	.7	.7	.55
Ca	3	2	.05	Dy	.6	.6	<.2
Ti	.5	.7	.4	Ho	.3	1.1	<.02
V	.5	.6	.4	Er	2	3.5	<.04
Cr	4	9	.4	Tm	<.2	<.2	<.03
Mn	.2	.1	≤2	Yb	<.3	.3	≤1.2
Fe	8.2	25.5	12.0	Lu	.8	1	11
Co	<.06	<.06	.2	Ta	3	2	.2
Ni	<3	1	<3	W	2	9	15

^aPpm by weight.

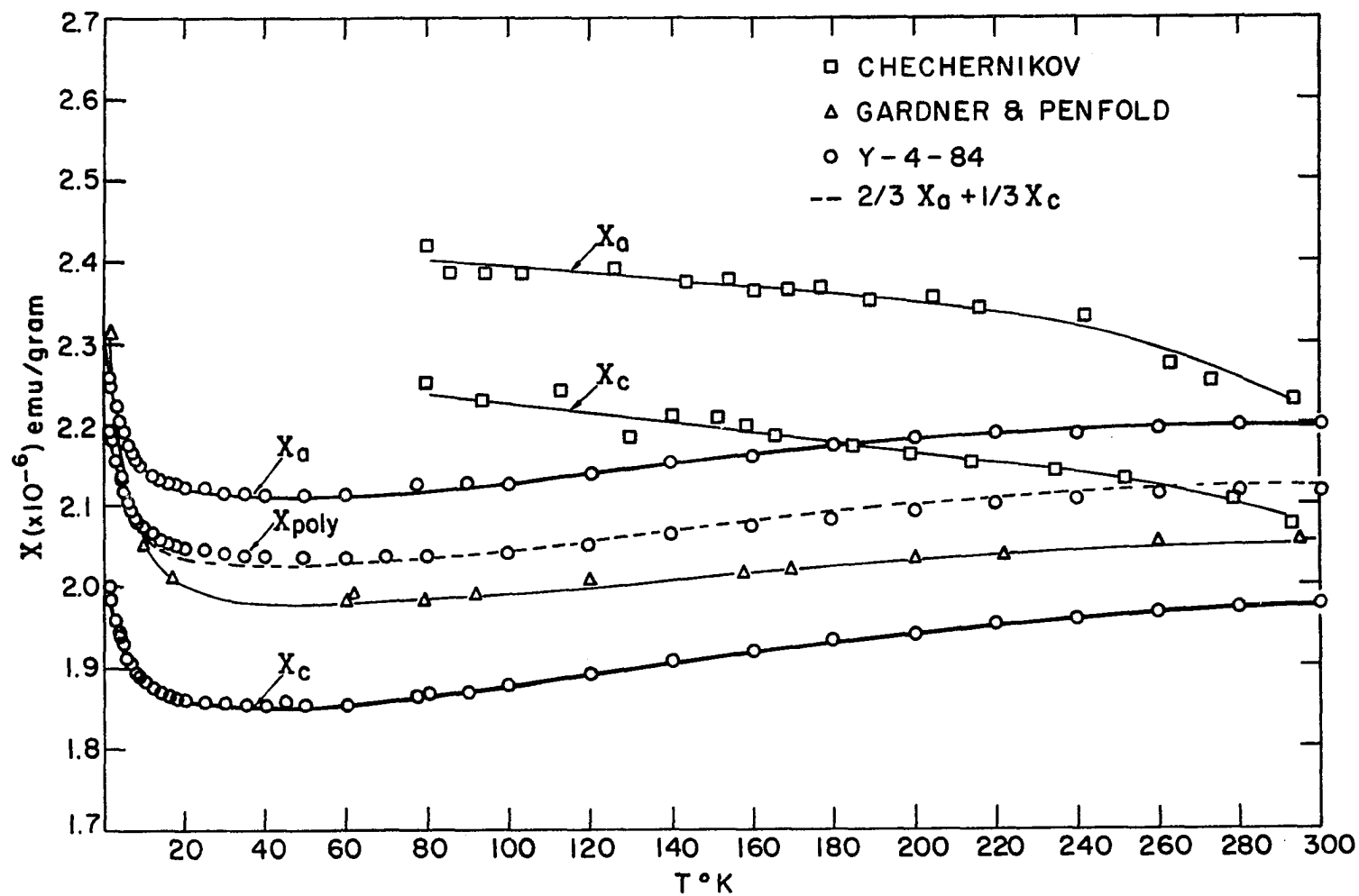


Fig. 27. Magnetic susceptibility of single and polycrystalline yttrium metal.

scandium, lanthanum and lutetium. The susceptibility of yttrium was found to be paramagnetic with a slightly positive temperature dependence above 40°K. Below 10°K the susceptibility increases rather sharply but less so than the previously reported data by Gardner and Penfold.²¹ Their polycrystalline data were approximately 3% lower than that found in this study and had a slightly less positive temperature dependence below 150°K. The weighted average of the single crystal data for sample 4-84, shown by the dashed curve in Fig. 27, were found to agree quite well with that of the polycrystalline specimen. In agreement with Chechernikov et al.,²³ the susceptibility along the "a" axis was greater than that along the "c" axis.

Good agreement was found between the experimental data for crystals 4-84 and 4-170 over the entire temperature range measured, although 4-170 had a slightly lower susceptibility, presumably due to the presence of greater amounts of gaseous impurities. Likewise the data for polycrystalline 4-170 were found to agree quite well with the weighted average of the single crystal data.

Whereas well characterized high purity yttrium such as 4-84 and 4-170 behaved as described above, the susceptibility of samples prepared from a third batch of metal, 4-85, was found to behave anomalously. The data for a single crystal, 4-85-A, were found to agree almost exactly with crystal 4-170 at higher temperatures but below approximately 80°K an anomalous temperature dependence was observed. The data for this crystal

are shown in Fig. 28 along with that of 4-84. To verify these results a second crystal, 4-85-B, was grown from the same stock metal and the same results were found. A polycrystalline specimen of 4-85 was also measured and, above 80°K, its susceptibility found to be approximately 1.5% higher than would be expected from the weighted average of the single crystal data. In addition the anomalous increase in the susceptibility at approximately 80°K was not observed. The behavior of this crystal suggested some type of magnetic ordering due to the presence of impurities. Therefore careful field dependent measurements were made from 60°K to below liquid helium temperatures. However, within experimental error, no field dependence of the susceptibility was found in either the single or polycrystalline sample above 5°K. The discrepancy between the single and polycrystalline data probably results from the different heat treatment given the two specimens. The single crystal was grown at 1350°K for 30 hours whereas the polycrystalline sample was arc melted, rolled 20% and annealed at 725°K for 24 hours to bring about random recrystallization. The impurity which is expected to be causing this behavior may be more randomly distributed in the single crystal and hence does not order until 80°K. On the other hand, the low temperature recrystallization may have resulted in fairly large precipitates in the polycrystalline specimen which order at a much higher temperature. Photomicrographs of both polycrystalline 4-84 and 4-85 as well as single crystal 4-84 are shown in

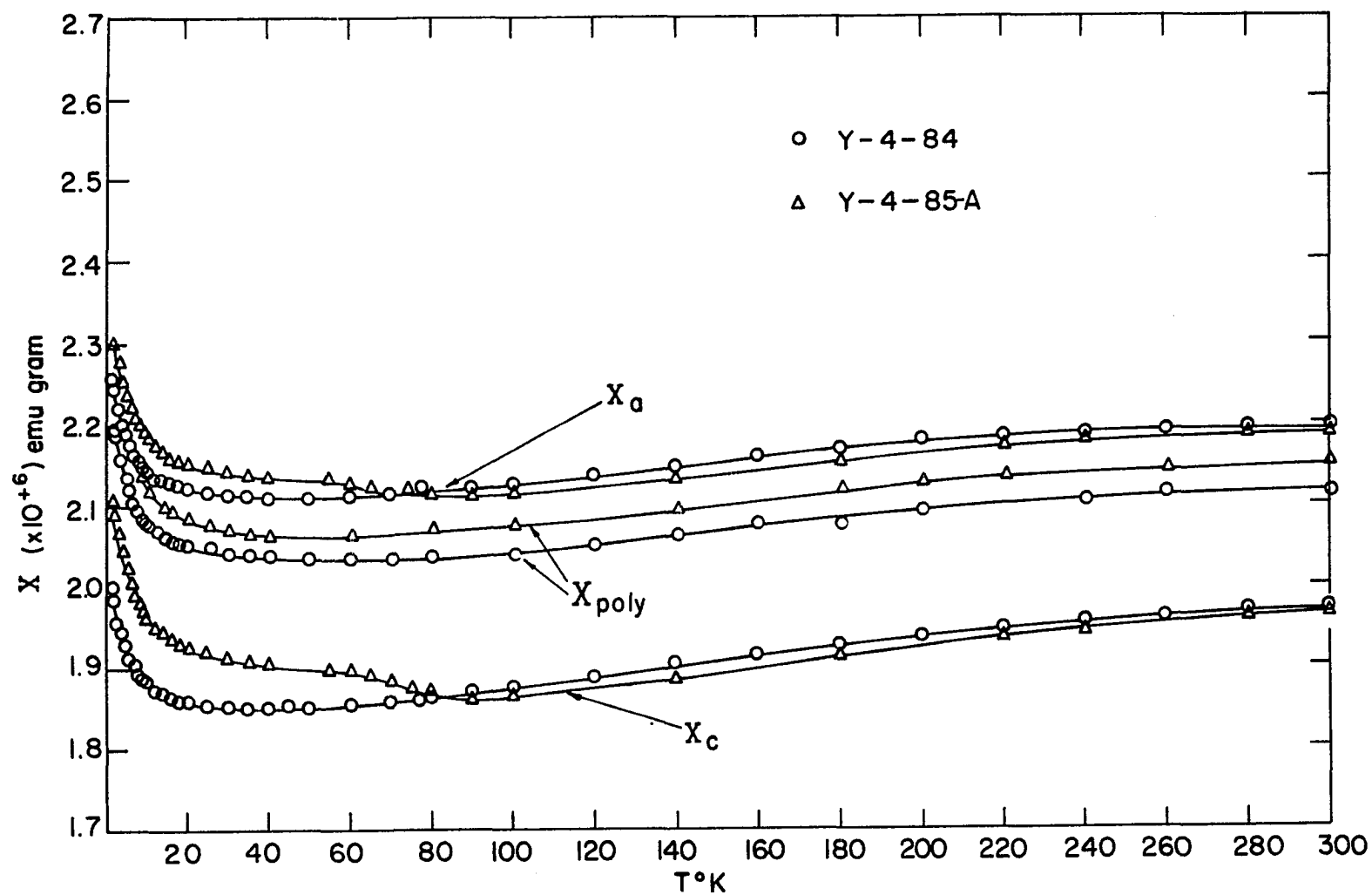
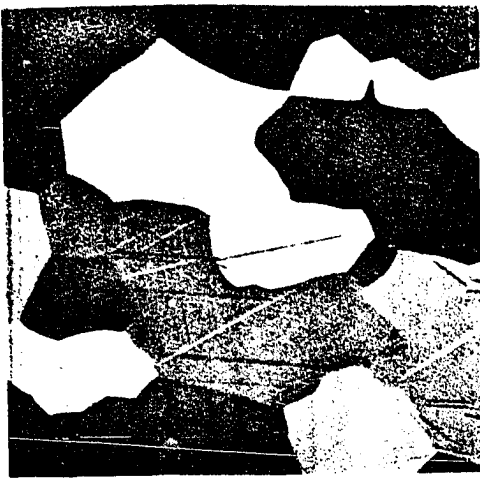


Fig. 28. Comparison of the susceptibilities of yttrium single crystals 4-84 and 4-85-A.

Fig. 29 and tend to support this theory. Whereas polycrystalline sample 4-84 had a very clean microstructure, both single and polycrystalline 4-85 contained second phase precipitates. The precipitates in the polycrystalline sample were located in the grain boundaries and were noticeably larger and more numerous than in the single crystal. Iron would seem to be the most likely impurity due to its high Curie temperature. As noted in Table IX this metal did contain more iron than either 4-84 or 4-170. Furthermore a sample doped with .13 a/o iron, shown in Fig. 31, was found to have an anomalous increase in the susceptibility at roughly the same temperature. However this sample exhibited field dependence over the entire temperature range while none was detected above liquid helium temperature in either of the 4-85 samples. It is of course possible that the amount of ordering needed to account for this behavior is quite small and was not detected by field dependence. A microprobe analysis of the polycrystalline sample found the precipitates to be primarily yttrium oxide with a few ppm of dysprosium oxide. It is concluded that the anomalous susceptibility found in this batch of metal is not completely understood. However the results are shown for completeness.

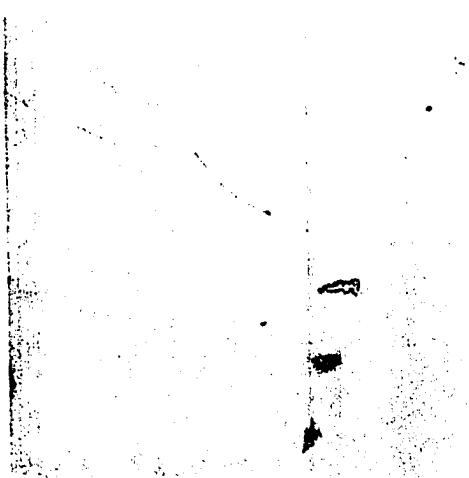
As shown in Fig. 30 the magnetic anisotropy of single crystal yttrium is almost linear with temperature and increases approximately 18% between 300 and 1.5°K. The anisotropy of both 4-85-A and 4-85-B were found to be somewhat lower than that for 4-84 below 85°K. Likewise the anisotropy of 4-170



(a)



(b)



(c)



(d)

Fig. 29. Photomicrographs of single and polycrystalline yttrium metal.

(a) Polarized light photomicrograph of polycrystalline Y-4-84, 100X. (b) Polarized light photomicrograph of polycrystalline Y-4-85, 100X. (c) Bright field photomicrograph of polycrystalline Y-4-85, 500X. (d) Bright field photomicrograph of single crystal Y-4-85, 500X.

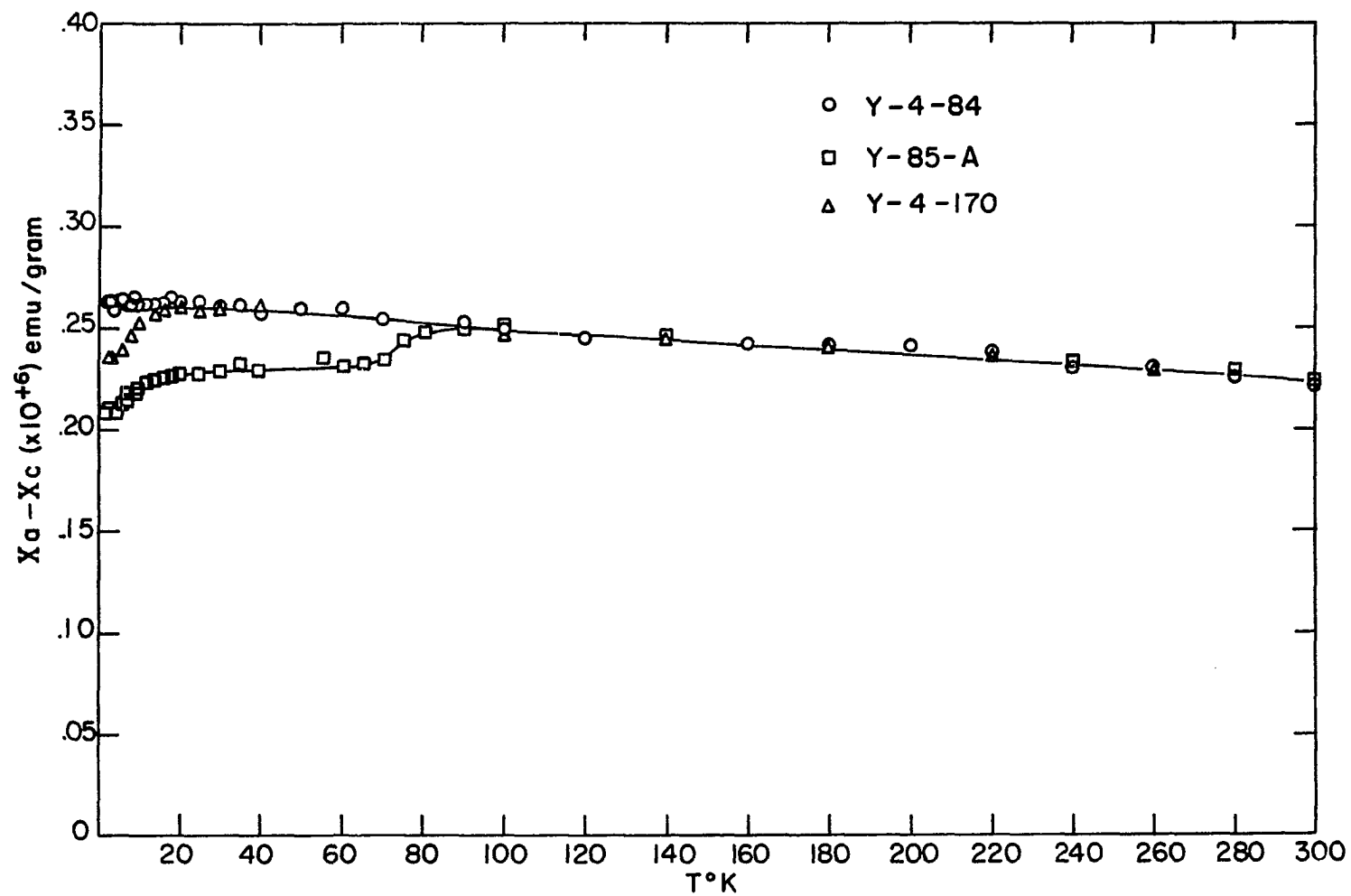


Fig. 30. Magnetic anisotropy versus temperature for single crystals of yttrium.

was revealed to be somewhat smaller than that of 4-84 below 15°K.

3. Susceptibility of yttrium alloys

Plots of susceptibility vs temperature for a number of polycrystalline yttrium samples doped with known amounts of impurities are shown in Fig. 31. These impurities included hydrogen, oxygen, iron and a mixture of rare earths. The samples were prepared as described in Section IV.A.4 and were recrystallized prior to their measurement. As discussed in Section V.A.3, the effects of these impurities must be viewed in light of their disposition in the metal, i.e. whether or not they are in solution or exist as second phase precipitates.

a. Yttrium-hydrogen At room temperature the addition of 4.3 a/o hydrogen lowered the susceptibility of yttrium by 1.29% or by .30% per atomic per cent hydrogen. This reduction is somewhat lower than for scandium where 1 a/o hydrogen lowered the susceptibility by 2.36%. Metallographic examination of this sample revealed that some second phase did exist, indicating that the room temperature solubility limit had been exceeded. Thus the suppression of the susceptibility per a/o hydrogen is most likely larger than the above value over the solid solution range.

b. Yttrium-oxygen The addition of 1.75 a/o oxygen lowered the room temperature susceptibility of yttrium by 2.52% or by 1.44% per a/o oxygen. As with hydrogen, the suppression of the susceptibility per a/o of solute, was somewhat lower

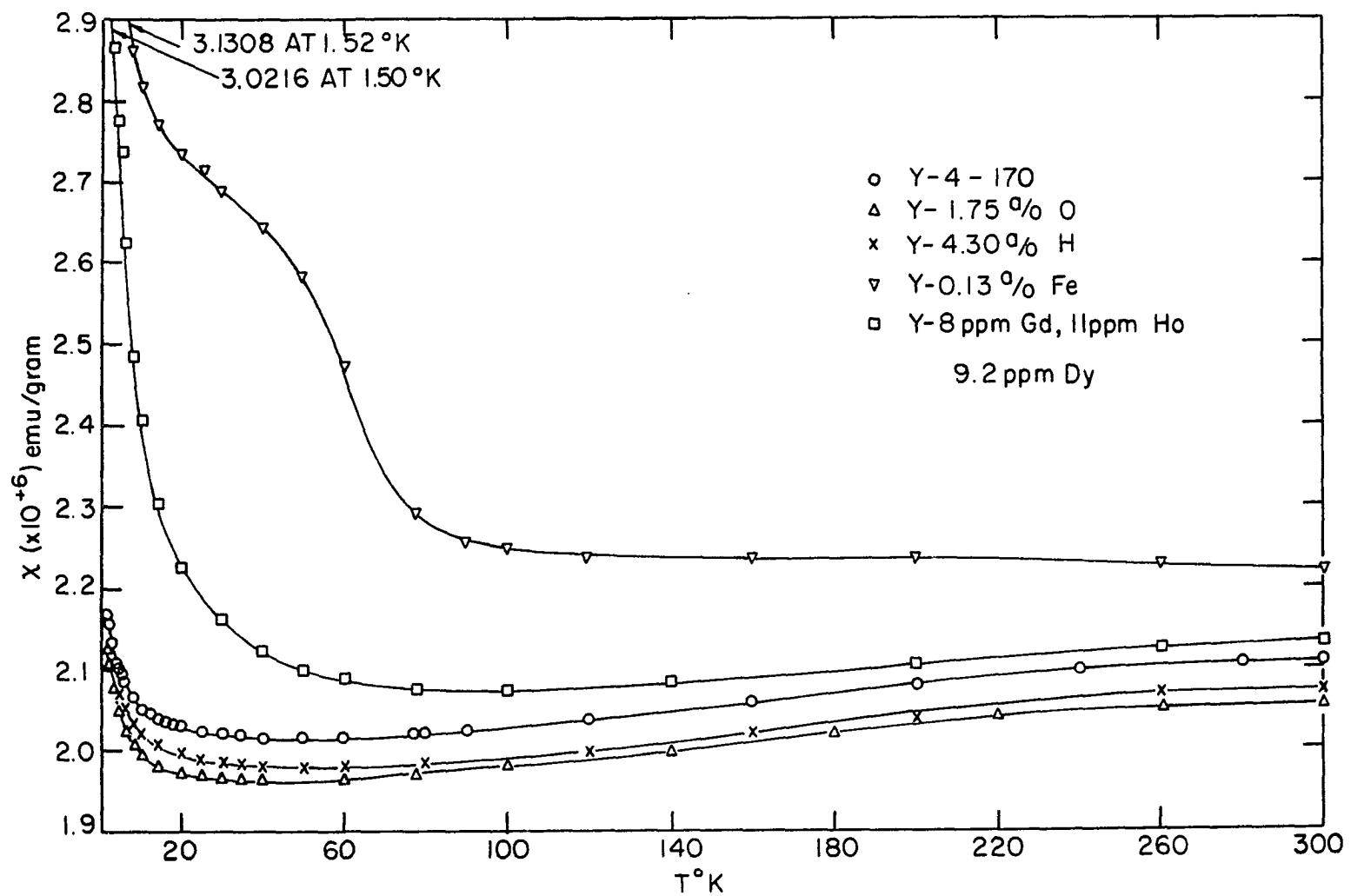


Fig. 31. The effect of a number of dilute impurities on the susceptibility of polycrystalline yttrium.

than the comparable value in scandium. A metallographic examination, however, revealed that the sample contained considerable second phase. Since the solubility limit of oxygen at room temperature was obviously exceeded the amount of reduction per a/o solute is likely higher than the above value.

c. Yttrium-iron The addition of .13 a/o iron increased the susceptibility of yttrium as shown in Fig. 31. The temperature dependence of the susceptibility was found to be somewhat anomalous, the data being almost linear to approximately 70°K and then rising rather sharply. This behavior suggested that at least part of the iron was ordering since paramagnetic impurities would not behave in this manner. Field dependence measurements confirmed the presence of magnetic ordering. This sample exhibited field dependence even at room temperature which would indicate that at least part of the iron had not gone into solution and existed as iron rich clusters, probably intermetallic compounds. Metallographic examination revealed the presence of small second phase precipitates, the bulk of which were located in the grain boundaries. The field dependent moment at 1.54, 30, 60 and 300°K was .01047, .00633, .00436 and .00220 emu/gram respectively. These moments correspond to 47.6, 28.8, 19.8 and 10 ppm of saturated iron. These data indicate that the bulk of the iron was in solution since these moments correspond to only a fraction of the total iron present.

d. Yttrium-rare earth impurities A sample found by mass spectrograph analysis to contain 8 ppm gadolinium, 9.2 ppm dysprosium, and 11 ppm holmium was measured and its susceptibility shown in Fig. 31. No field dependence was observed in this sample above liquid helium temperatures. At the lowest temperature measured, 1.54°K, the field dependent moment was .0065 emu/gram which would correspond to 27 ppm saturated gadolinium if this were the only impurity present.

After subtracting off the susceptibility of the pure yttrium the average effective moment of the impurities was calculated from a plot of reciprocal susceptibility vs temperature. The data were found to obey a Curie Weiss law with an effective moment of 10.47 ± 1.24 and a paramagnetic Curie temperature of -2.4°K. The theoretical moment of the weighted average of these impurities is $9.85 \mu_B$. However due to the range of values for the effective moment, resulting from the $\pm 20\%$ accuracy of the mass spectrograph analysis, it is not possible to say that the average moment is enhanced above the free ion value. However the data do indicate that if enhancement does occur it is not by more than 10 or 15%.

C. Lanthanum

1. Sample purity

Three polycrystalline samples designated 4-133, 4-184-A and 4-184-B, were prepared from two separate batches of metal. The analyses of these samples are given in Table X in ppm

Table X. Analyses of lanthanum metal.

Element	4-133	4-184-A	Element	4-133	4-184-A
H	1894(14) ^a	413(3)	Cu	3	3
C	358(31)	277(24)	Sc	.3	≤ .4
N	181(18)	218(22)	Y	10	2.8
O	916(106)	330(38)	Ce	≤10	20
F	88(12)	190(26)	Pr	<.3	.7
Na	3	1	Nc	10	<.5
Mg	<.3	<.4	Sm	<.3	<.3
Al	4	<2	Eu	<.1	<.2
Si	5	<1	Gd	6	2.4
Cl	20	4	Tb	≤2	.8
Ca	.8	.4	Dy	<.3	.4
Tl	2	.1	Ho	<.3	3
V	.3	.09	Er	<.6	1.1
Cr	.7	1	Tm	<.06	<.06
Mn	.1	≤6	Yb	<.3	<.5
Fe	5.7	6.5	Lu	≤1	<.1
Co	<.06	≤.5	Ta	10	2
Ni	3	1	W	<1	<2

^aPpm by weight.

atomic. Any element not listed was found to be present in a concentration of less than 1 ppm. Both 4-184-A and 4-184-B were prepared from the same stock metal and, due to the close agreement between their susceptibilities, are assumed to have the same analysis. Samples 4-184-A and B and 4-133 were found to have field dependent moments of .00078 and .00101 emu/gram which would correspond to 2.9 and 3.8 ppm of saturated gadolinium if this were the only impurity present.

The susceptibility data for lanthanum below 6°K are not believed to be as accurate as for the other elements measured due to interference from superconductivity. When changing temperatures a slight drift in the recorder, believed due to convection currents, was noted. This was especially pronounced at low temperatures but was corrected for by zeroing the recorder after each temperature change. However this was impossible for lanthanum at low temperatures because of the erratic behavior of the balance when the field was reduced to zero, allowing the sample to go superconducting.

2. Susceptibility of dhcp lanthanum

A plot of magnetic susceptibility vs temperature for the purest lanthanum sample, 4-184-A, is shown in Fig. 32 along with results previously reported by Lock²⁵ and Wohlleben.¹² The data for this same sample are also shown in Fig. 41 along with that found in this investigation for scandium, yttrium and lutetium.

Polycrystalline dhcp lanthanum was found to be para-

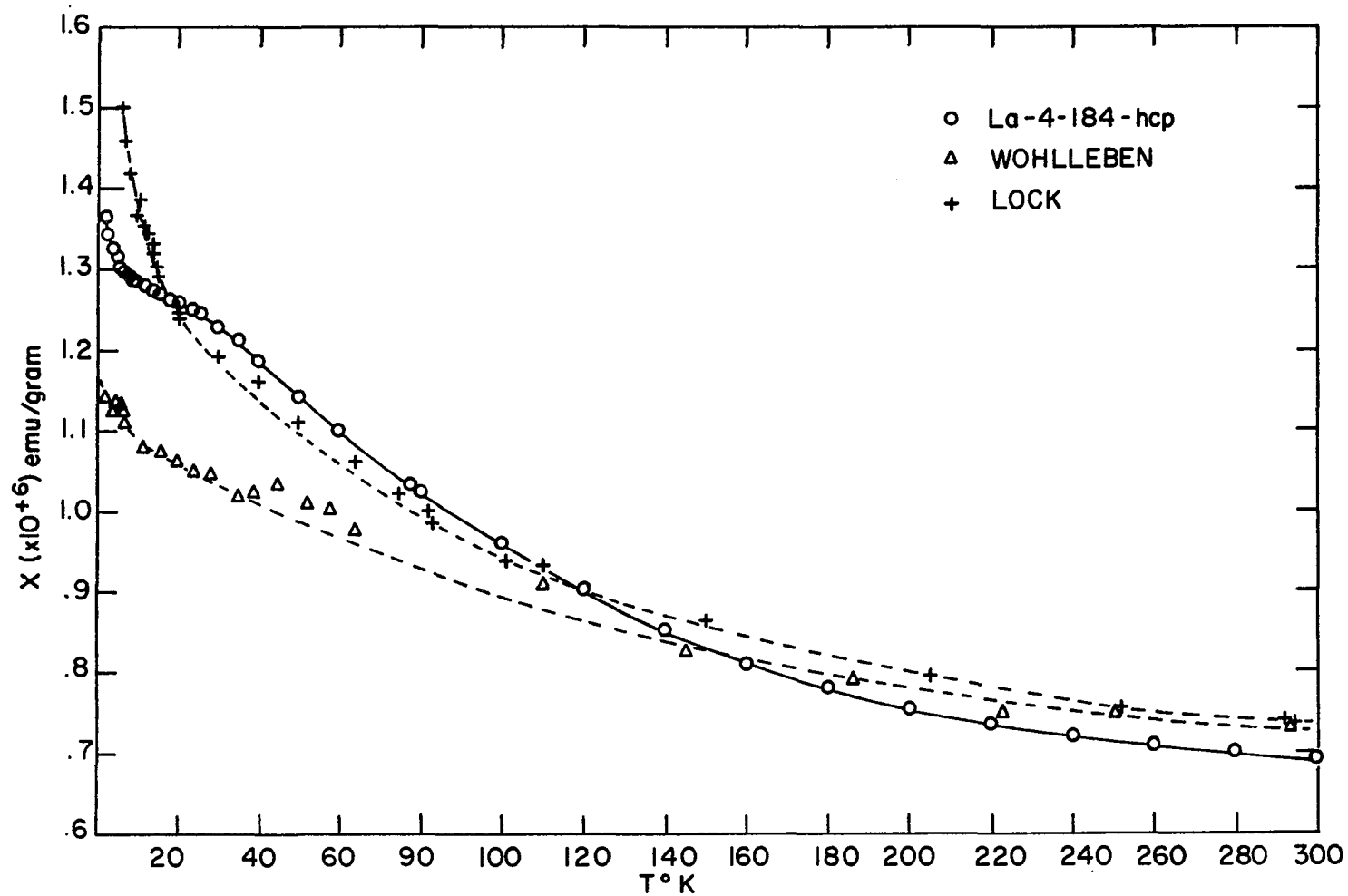


Fig. 32. Magnetic susceptibility of polycrystalline dhcp lanthanum metal.

magnetic with a temperature dependence approximately $1/3$ that of scandium on a gram basis. For sample 4-184-A the room temperature susceptibility was $.6911 \times 10^{-6}$ emu/gram and rose to a high of 1.3749×10^{-6} emu/gram at 1.5°K . As shown in Fig. 32 the data appear almost parabolic to approximately 30°K where a significant change in slope occurs. Sample 4-84-B showed similar behavior. A plot of reciprocal susceptibility vs temperature is shown in Fig. 33 and shows Curie-Weiss behavior between 30° and 160°K . The effective moment and paramagnetic Curie-Weiss temperature calculated from the data over this temperature range were $.58 \mu_B$ and -216°K respectively. This moment is roughly $1/3$ the value of $1.647 \mu_B$ found for scandium. Above 160°K the slope of the Curie-Weiss plot decreased, suggesting that the moment may be larger at higher temperatures.

The susceptibility of the second polycrystalline sample, 4-133, is shown in Fig. 34. The susceptibility of this specimen was .52% lower than that of 4-184-A at room temperature and 1.59% lower at 10°K . From the results of the following section, this somewhat lower susceptibility is believed due primarily to .19 a/o hydrogen in the sample. Other impurities included .036 a/o oxygen, .036 a/o carbon and .019 a/o nitrogen.

3. Susceptibility of lanthanum alloys

Plots of susceptibility vs temperature for a number of polycrystalline dhcp samples doped with known amounts of

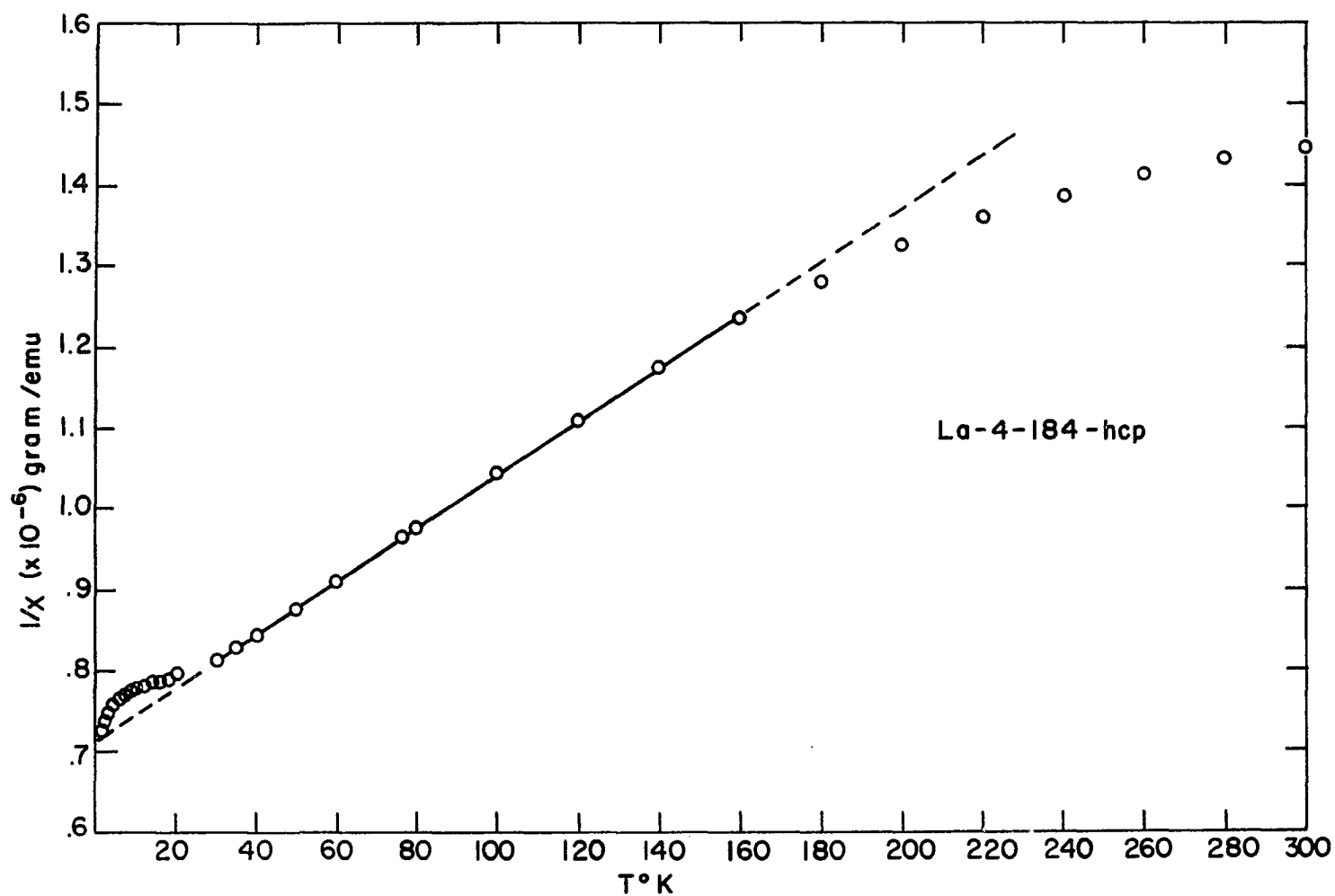


Fig. 33. Plot of reciprocal susceptibility versus temperature for polycrystalline dhcp lanthanum.

hydrogen and oxygen are shown in Fig. 34. All of these samples were prepared from the same stock metal as 4-84 and were prepared as described in Section IV.A.4. Debye Scherrer X-ray patterns were taken of all the samples and within the accuracy of this technique, all were found to be pure dhcp. The samples were also examined metallographically to determine the extent of solubility of the solute. In general these data revealed that while the solubility of hydrogen and oxygen in lanthanum is quite low, its susceptibility is very sensitive to the addition of these nonmagnetic impurities, even more so than for scandium.

a. Lanthanum-hydrogen At room temperature 1.90 a/o hydrogen lowered the susceptibility by 1.24%. At lower temperatures the suppression was somewhat greater, namely 6.96 and 8.33% at 77 and 10°K respectively. Metallographic examination revealed that the solubility limit of hydrogen had been exceeded, the photomicrograph showing extensive second phase precipitates. If we assume that only the hydrogen in solution has any major affect on the susceptibility, then the actual lowering per a/o solute is probably greater than that determined from the above data. The similarity between the susceptibilities of this specimen and sample 4-133, which contained .19 a/o hydrogen, are noted.

b. Lanthanum-oxygen Unlike hydrogen, the addition of oxygen was found to lower the susceptibility more equally over the entire temperature range. A series of alloys containing

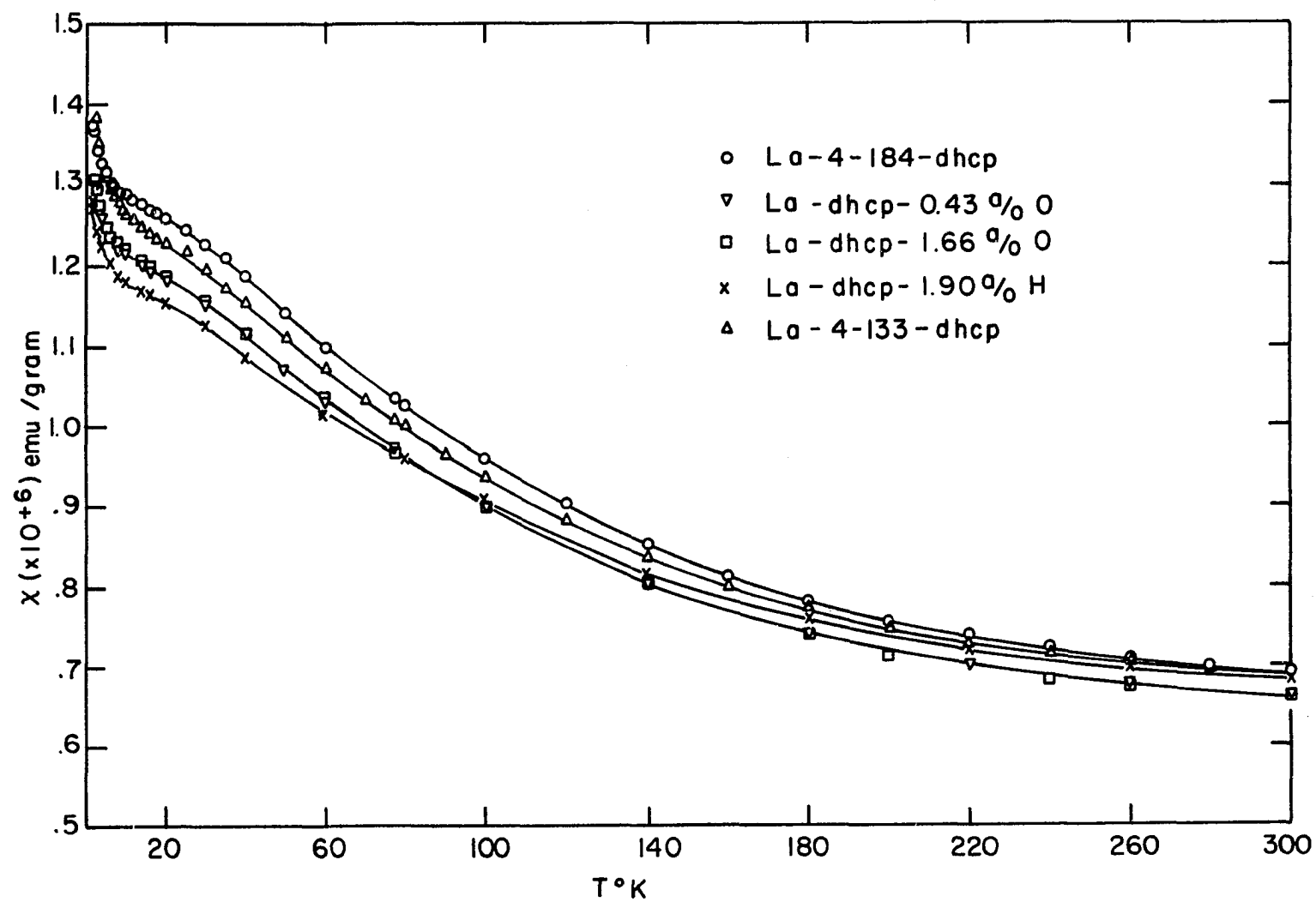


Fig. 34. The effect of dilute hydrogen and oxygen on the susceptibility of polycrystalline dhcp lanthanum.

.31 a/o, .43 a/o, .81 a/o and 1.66 a/o oxygen were measured and all were found to reduce the susceptibility by almost the same amount. At room temperature the amount of lowering was 3.62%, 4.04%, 4.01% and 4.79% for the four alloys respectively. The susceptibility of the alloys containing .43 a/o and 1.66 a/o oxygen are shown in Fig. 43 along with that of pure lanthanum. The susceptibility of the .81 a/o oxygen alloy was measured at room temperature only.

Since the suppression was approximately the same for all of the alloys it would seem that the solubility of oxygen in lanthanum is quite low and is exceeded even at .31 a/o. Photomicrographs of these alloys confirmed this, even the most dilute showing fine, evenly spaced precipitates. This would indicate, as expected, that the marked lowering of the susceptibility is brought about by only those oxygen atoms in solution. Any additional oxygen beyond the solubility limit forms precipitates and hence affects the susceptibility only as bulk La_2O_3 .

4. Susceptibility of fcc lanthanum

In an attempt to explain the difference between the data found in this investigation and that found by Lock²⁵ and Wohleben,¹² a study of fcc lanthanum was made. In the past a number of investigators have reported measuring various physical properties of pure fcc lanthanum. However it is doubtful that their samples were very pure since as higher purity lanthanum became available it became increasingly more difficult to obtain pure fcc samples. Despite repeated efforts, samples

prepared from metal 4-184 were found to be almost pure dhcp after a variety of straining and quenching processes.

Initially it was felt that this high temperature phase stabilization was caused by hydrogen. Consequently the alloyed specimen containing 1.90 a/o hydrogen was given a treatment designed to stabilize the fcc phase at room temperature. After sealing the specimen in a tantalum envelope under 2/3 atmosphere of argon, the envelope was rolled to obtain good thermal contact, heated to approximately 400°K for 15 minutes and then quenched in ice water. A Debye Scherrer pattern revealed that the sample was still pure dhcp.

Identical treatment was then carried out on the four oxygenated samples. Debye Scherrer patterns found only the 1.66 a/o oxygen sample to be fcc. The .81 a/o oxygen alloy was found to be a mixture of the two phases while the two more dilute alloys were still pure dhcp.

The susceptibility of the fcc (1.66 a/o) sample was measured from 1.5 - 300°K and these results are shown in Fig. 35. When compared with the dhcp alloy the structure change was found to raise the room temperature susceptibility by roughly 10% while leaving the lower temperature data almost unchanged. Assuming that the oxygen has the same effect in both the dhcp and fcc phase, then a room temperature value of approximately $.756 \times 10^{-6}$ emu/gram is obtained for fcc lanthanum having the same purity as sample 4-184. The estimated susceptibility of fcc lanthanum from 1.5 to 300°K is shown in Fig. 35 along with that for dhcp lanthanum.

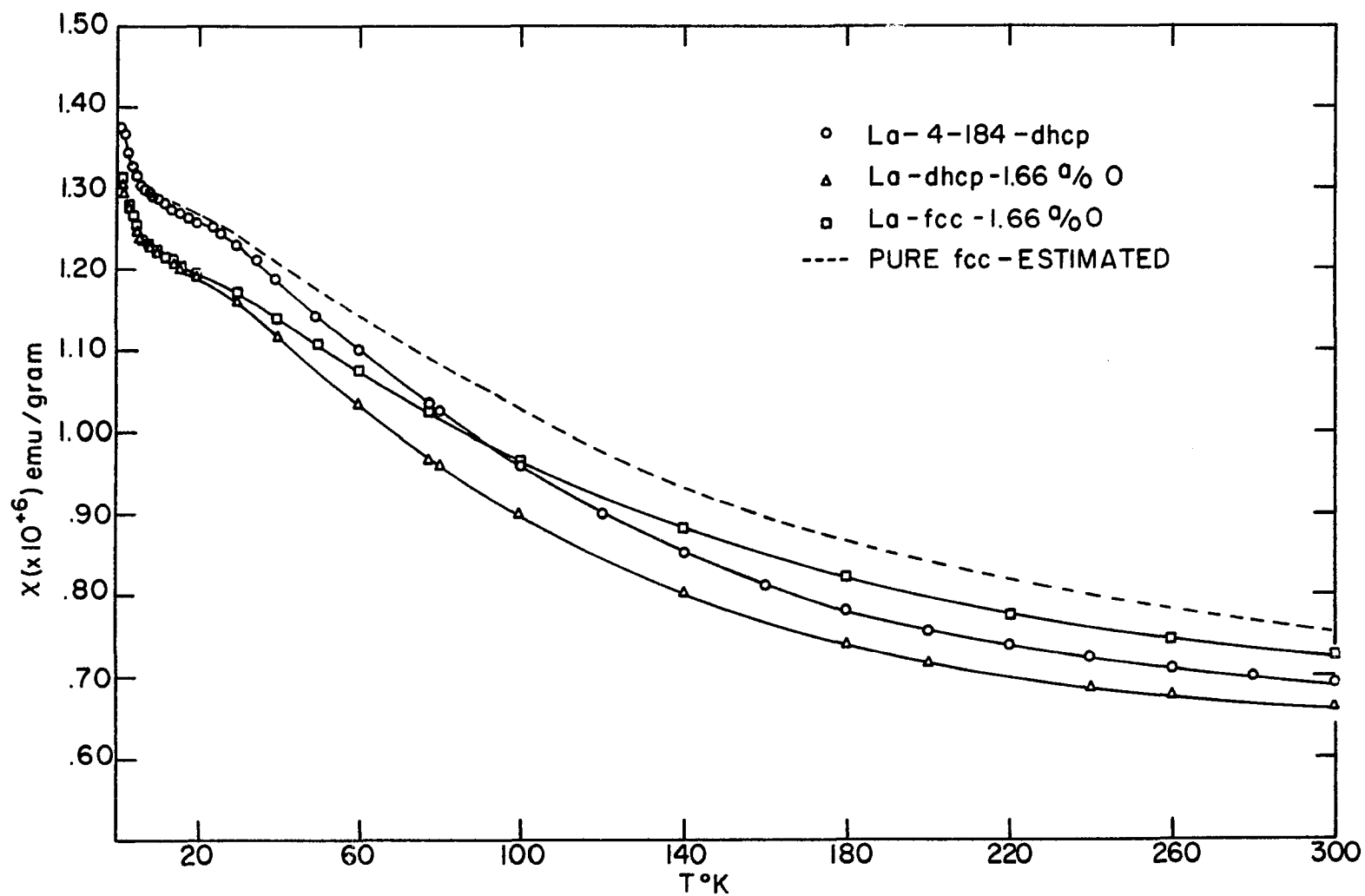


Fig. 35. Magnetic susceptibility of pure dhcp lanthanum and that of dhcp and fcc lanthanum containing 1.66 a/o oxygen. The dashed line is an estimate of pure fcc lanthanum.

A comparison of the susceptibility of the fcc sample containing 1.66 at.% oxygen with the data previously reported by Lock²⁵ is shown in Fig. 36. As noted, quite good agreement was observed over the entire temperature range. However Lock did report that his samples were predominately dhcp. The somewhat lower temperature dependence found by Wohlleben¹² is difficult to explain, although the addition of hydrogen to fcc lanthanum could possibly result in such a temperature dependence. As noted above, the addition of hydrogen to dhcp lanthanum lowered the susceptibility more at low than at high temperatures.

D. Lutetium

1. Sample purity

Three single crystals designated 4-106, 4-177 and 4-187 were prepared from three separate batches of metal and a fourth (4-157) was obtained from Tonnie and Gschneidner.³⁶ This latter crystal had been used to measure the elastic constants and was known to contain a fair amount of rare earth impurities, including 56 ppm gadolinium. The analyses of these crystals are listed in Table XI in ppm atomic. Any impurity not listed was found to be present in a concentration of less than 1 ppm. As with scandium and yttrium all the polycrystalline specimens were prepared from part of their corresponding single crystal and hence are assumed to have the same analysis.

Isotherms of moment vs magnetic field for polycrystalline

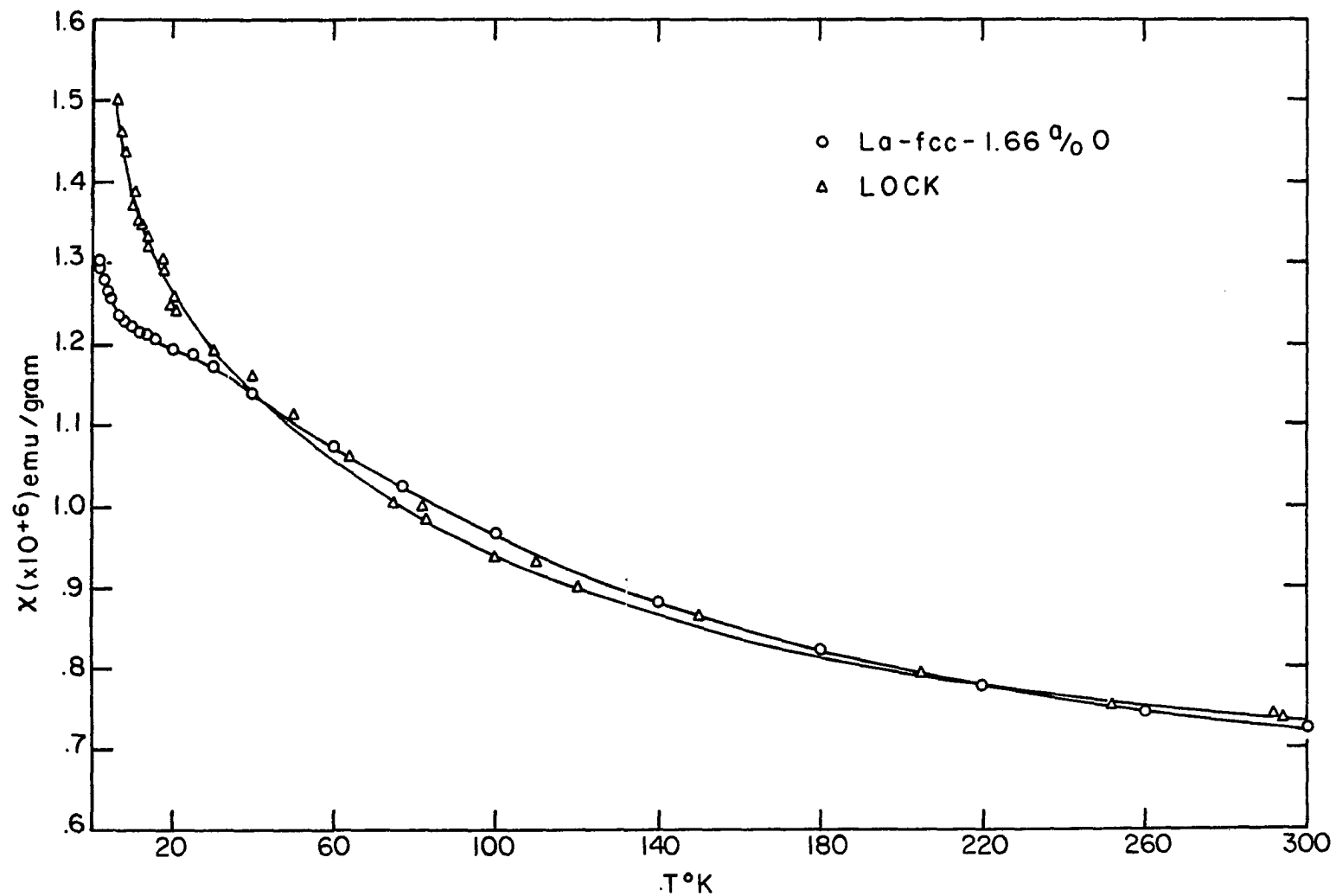


Fig. 36. The susceptibility of an fcc lanthanum-1.66 a/o oxygen alloy and a dhcp lanthanum sample reported by Lock.

Table XI. Analysis of lutetium metal in ppm atomic

Impur- ity	4-106	4-157	4-177	4-187	Ele- ment	4-106	4-157	4-177	4-187
H	2256(13) ^a	607(3.5)	52(.3)	(1215)(7)	Cu	6	60	<1	30
C	990(68)	496(34)	218(15)	(714)(49)	Sc	2	<.5	≤4	1
N	162(13)	125(10)	12.5(1)	625(50)	Y	1.9	27	1.0	<1
O	2351(215)	1870(171)	448(41)	2679(245)	La	8.6	.6	12	14
F	55(6)	46(5)	<3(<3)	<3(<3)	Ce	.6	3.5	.93	2.1
Na	.2	8	<6	10	Pr	1.5	1	.55	1.0
Mg	.4	<.5	<.4	<.4	Nd	.6	2	.1	≤.2
Al	7	10	≤5	2	Sm	<.3	<.4	.06	≤.8
Si	≤2	5	3	2	Eu	<.2	<.3	<.2	≤.6
Cl	1	30	.8	7	Gd	.2	56	2.5	.92
Ca	1	.8	1	.9	Tb	.5	10	.47	.91
Ti	1	≤1	2	10	Dy	.6	2.8	≤2.4	≤.6
V	≤.06	≤4	.8	2	Ho	.7	3.0	.24	<.04
Cr	.9	6	2	1	Er	3.2	16	3.8	≤15
Mn	<.1	<.06	.4	<.4	Tm	.07	<.2	.04	≤.3
Fe	17	87.7	22	24	Yb	<.3	<.3	.2	<.3
Co	<.1	≤5	.3	≤.6	Ta	40	80	3	90
Ni	18	8.9	11.9	12	W	N.D.	1	30	4

^aPpm by weight.

samples 4-106, 4-177 and 4-157 at the lowest temperatures measured are shown in Fig. 37. The field dependent moments for the three samples were .00031, .00115 and .01359 emu/gram respectively. These moments could be accounted for by 1.2, 4.3 and 50.7 ppm of saturated gadolinium assuming this was the only impurity present. The field dependence, and hence the relative purity, of sample 4-187 was almost identical to sample 4-106.

2. Susceptibility of pure lutetium

Plots of susceptibility vs temperature for samples 4-106, 4-177 and 4-157 are shown in Fig. 38. The same data for crystal 4-106 are shown in Fig. 41 along with that for scandium, yttrium and lanthanum found in this investigation.

The susceptibility of lutetium was found to be paramagnetic with a slight maxima centered at about 120°K. The room temperature susceptibility of polycrystalline sample 4-106 was 1.0400×10^{-6} emu/gram or approximately 33% higher than the purest lanthanum sample. The data increased to a maximum of 1.0987×10^{-6} emu/gram at 120°K and then decreased to 1.0712×10^{-6} emu/gram at 14°K. At lower temperatures a slight increase, believed to reflect the presence of paramagnetic impurities, was again observed. This increase for sample 4-106 was less than for any of the specimens of the four metals measured.

Good agreement was observed between samples 4-106 and 4-187 over the entire temperature range. However the susceptibility of 4-177, as shown in Fig. 38, turned up more sharply

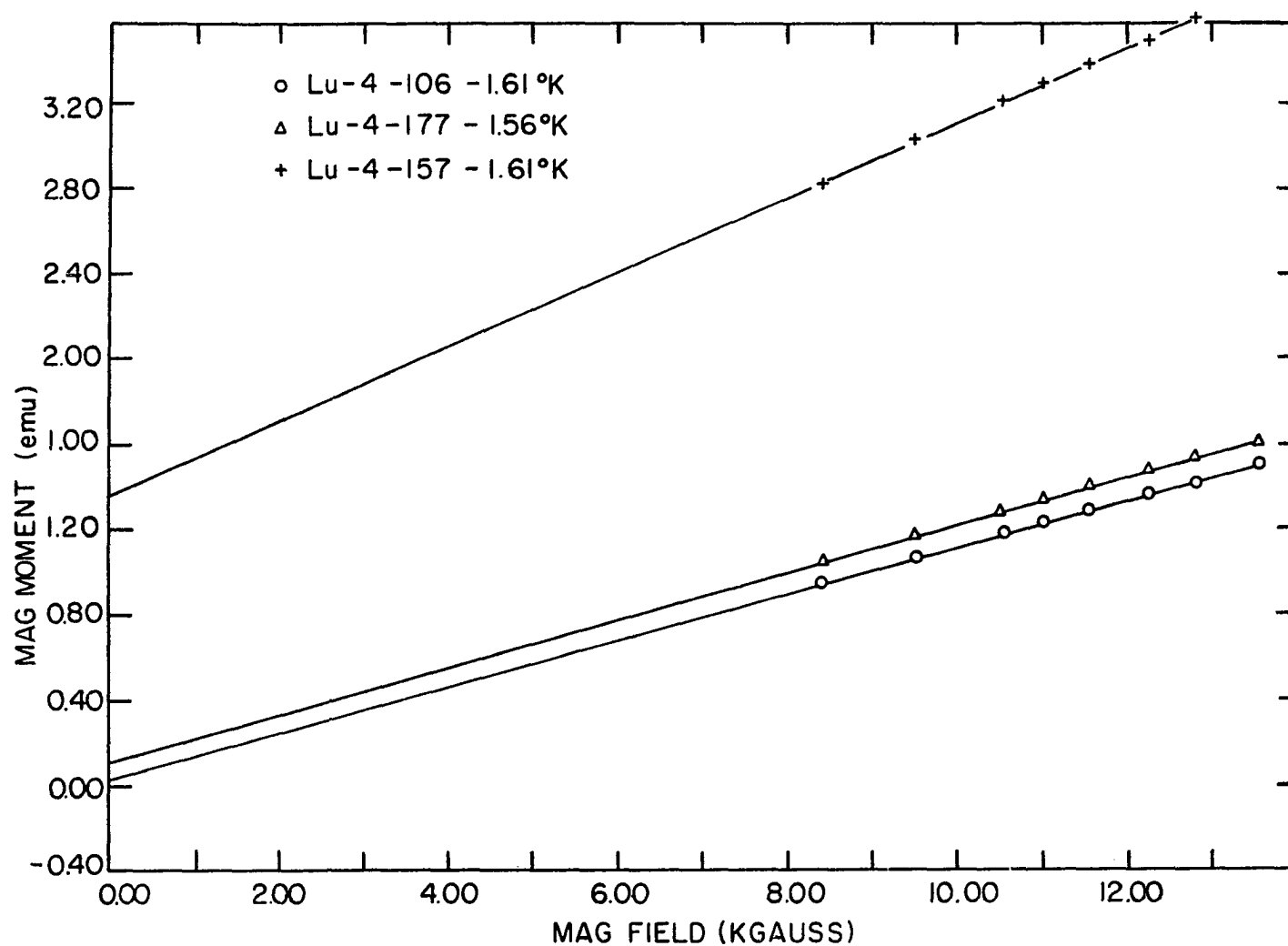


Fig. 37. Plots of magnetic moment versus field for several polycrystalline samples at the lowest temperature measured.

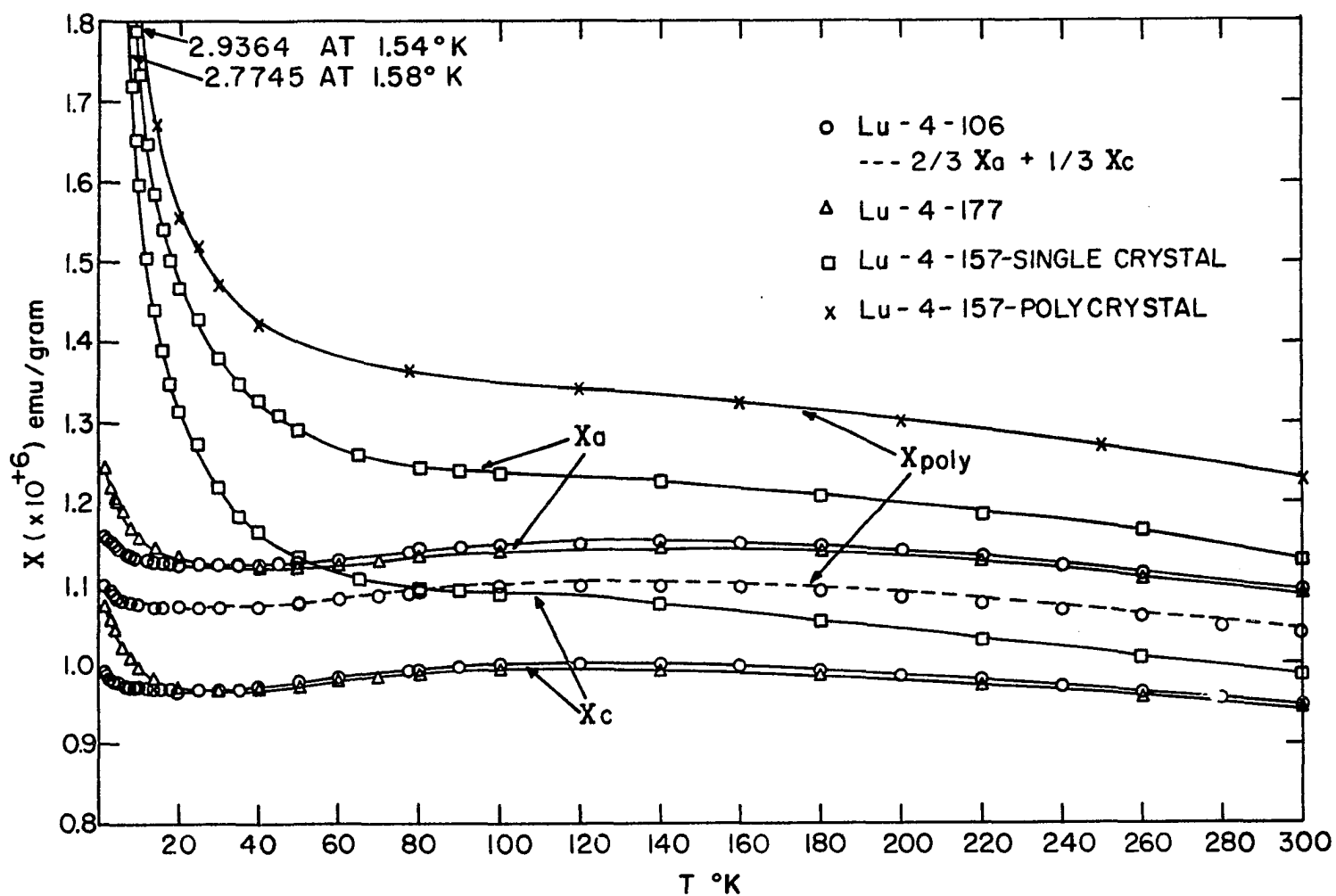


Fig. 38. Magnetic susceptibility of several single and polycrystalline samples of lutetium metal which contained varying amounts of impurities.

at low temperatures indicating a slightly larger amount of magnetic impurities. This is in agreement with the field dependence measurements which found this sample less pure relative to 4-106 or 4-187. At temperatures above 40°K the susceptibility of both single and polycrystalline 4-177 was approximately .8% lower than that of either 4-106 or 4-187 which would seem to indicate that these samples contained a higher concentration of nonmagnetic impurities. This is difficult to explain in light of its analysis which shows it to have a lower concentration of these impurities.

As with scandium and yttrium the susceptibility along the "a" axis was greater than that along the "c" axis. Likewise the weighted average of the single crystal data agreed well with the polycrystalline values with the exception of sample 4-157. The polycrystalline data for this metal were somewhat higher than expected and is believed to result from magnetic ordering of impurity clusters. Whereas no field dependence was observed in the single crystal above 20°K, a moment of .00206 emu/gram corresponding to 7.7 ppm of saturated gadolinium, was found in the polycrystalline specimen. This behavior was initially believed to result from the different heat treatment given the two specimens. Whereas the single crystal was grown by annealing at 1450°C for 30 hours, the polycrystalline specimen was arc melted, strained 20% and annealed at 675°C for 24 hours to bring about random recrystallization. It was thought that the high temperature anneal

apparently drove the magnetic impurities into solution while the low temperature anneal did not. However a subsequent anneal at 1350°C for 2 days resulted in no additional lowering of the susceptibility at room temperature. A metallographic examination of this sample revealed that almost no additional grain growth had occurred, apparently due to the absence of strain in the preannealed specimen. These data would seem to suggest that it is the presence of grain boundaries rather than the type of anneal which is responsible for the higher susceptibility in the polycrystalline sample. It is believed that the grain boundaries serve as nucleation sites for iron rich second phase precipitates, some of which are large enough to magnetically order even at room temperature. Iron is believed to be responsible primarily because these data correlate well with that of a lutetium sample doped with a known amount of iron. This polycrystalline sample, discussed in Section V.D.3, was also found to have a significant field dependence at room temperature. In contrast a sample doped with a mixture of rare earths had no field dependence above liquid helium temperature. Metallographic examination also revealed that the solubility of iron in lutetium at room temperature in an annealed polycrystalline sample is quite low. This coupled with the fairly large concentration of iron (88 ppm) in sample 4-157, would tend to result in clusters of iron solute at the grain boundaries. The lack of such nucleation sites in the single crystal specimen results in most of the iron remaining

in solution or in the form of very fine precipitates where it behaves paramagnetically until a much lower temperature.

In Fig. 39 are shown plots of magnetic anisotropy vs temperature for the four measured crystals. The anisotropy was found to be almost constant with temperature, rising only slightly below 40°K. For crystal 4-106 the anisotropy rose from a room temperature value of $.1461 \times 10^{-6}$ emu/gram to $.1681 \times 10^{-6}$ emu/gram at 1.5°K. Excellent agreement was found between all of the measured crystals above 20°K. Below this temperature the anisotropy of 4-157 showed somewhat anomalous behavior which is almost certainly due to the effects of impurities in this specimen. Sample 4-187 showed the same effect but to a much lesser degree.

3. Susceptibility of lutetium alloys

Shown in Fig. 40 are plots of susceptibility vs temperature for a number of polycrystalline samples doped with dilute amounts of hydrogen, oxygen, iron and a mixture of rare earths. All of the specimens were prepared as described in Section IV.A.4 and were recrystallized prior to being measured. All of these results are discussed in light of the microstructure of these alloys since the effect of impurities on the susceptibility is believed to be strongly dependent on whether they are in solution or as a second phase.

a. Lutetium-hydrogen Hydrogen was found to lower the susceptibility of lutetium more at room temperature than at lower temperature. The addition of 5.45 a/o hydrogen reduced

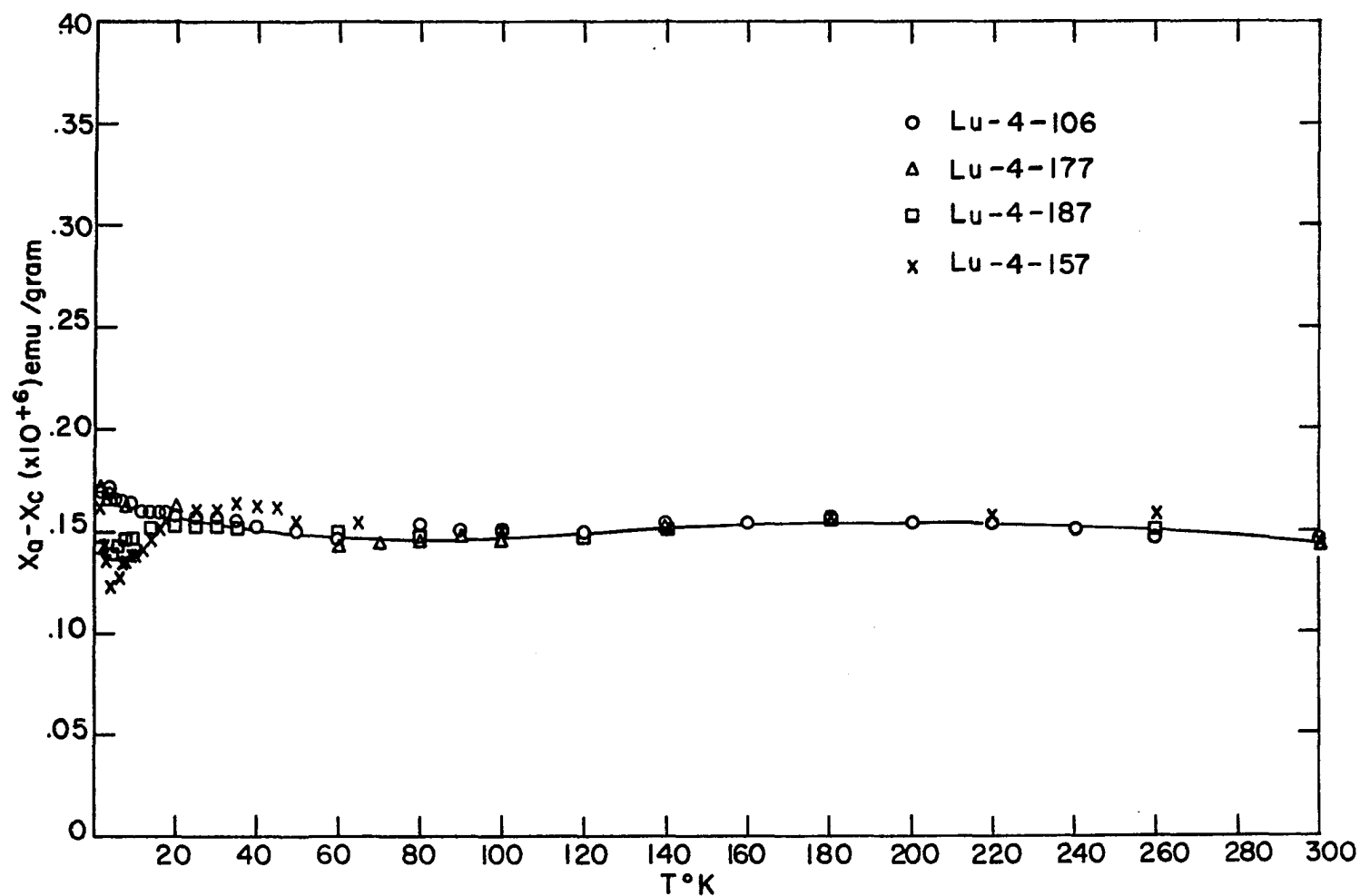


Fig. 39. Magnetic anisotropy versus temperature for single crystals of lutetium.

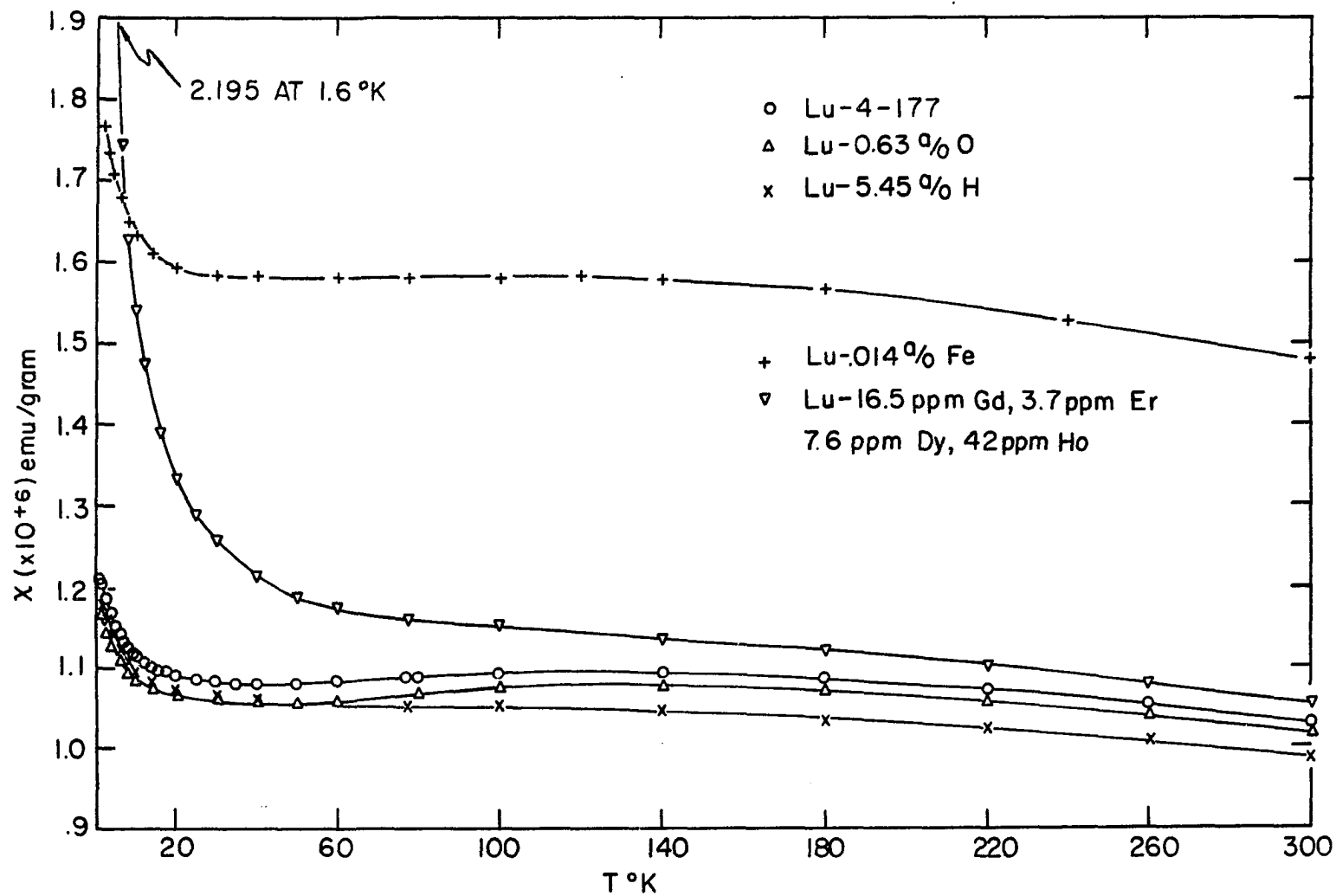


Fig. 40. Effect of a number of dilute impurities on the susceptibility of polycrystalline lutetium.

the room temperature susceptibility of lutetium by 4.24% but only 1.66% at 10°K. A photomicrograph of this alloy showed almost no second phase precipitates indicating that almost all of the hydrogen was in solution. Likewise a comparison of the lattice parameters of this sample with data by Bonnet and Daou⁴³ on the Lu-H system, indicated that the sample contained 5.5 a/o or 4.3 a/o hydrogen when compared with their "c" axis and "a" axis data respectively.

b. Lutetium-oxygen Unlike hydrogen, the addition of oxygen to lutetium was found to lower the susceptibility equally over the entire temperature range. Upon the addition of .63 a/o oxygen the room temperature susceptibility was suppressed by 1.25%. Metallographic examination revealed, however, that considerable second phase was present even at this low concentration of solute. The actual % lowering is therefore probably greater per a/o solute than the 1.98% value indicated from the above data.

c. Lutetium-tantalum The melting point solubility limit of tantalum in lutetium, 1.4 a/o, was found to have almost no affect on the susceptibility. The room temperature value actually increased slightly from 1.0339 to 1.0357×10^{-6} emu/gram. However considering the anisotropy remaining in these samples such a change is well within experimental error. Examination of this sample revealed that a large amount of second phase was present, indicating that for an arc melted sample, 1.4 a/o tantalum is well in excess of the solubility

limit. The similarity of the susceptibility of tantalum, namely $.850 \times 10^{-6}$ emu/gram at room temperature, with that of lutetium would result in very little lowering due to bulk undissolved tantalum.

d. Lutetium-iron A polycrystalline alloy containing .014 a/o iron was measured. Its susceptibility, shown in Fig. 40, is anomalously high at room temperature and increases only slightly between this temperature and 20°K. Below 20°K the susceptibility rises rather sharply. The field dependent moments at 1.6 and 300°K was .007 and .006 emu/gram respectively, indicating that a large amount of the iron was magnetically ordered. A metallographic examination revealed fine second phase precipitates, the bulk of which were located in the grain boundaries. These data clearly show that the solubility of iron is quite low and that the undissolved iron or iron rich precipitates are magnetically ordered. The sharp upturn below 20°K reflects the behavior of the dissolved iron which behaves paramagnetically until a much lower temperature.

e. Lutetium-rare earth impurities A sample found to contain 16.5 ppm gadolinium, 10 ppm dysprosium, 42 ppm holmium and 3.7 ppm erbium by mass spectrographic analysis was measured and its susceptibility shown in Fig. 40. After subtracting off the susceptibility of the pure lutetium, a plot of reciprocal susceptibility vs temperature was made. These data was found to obey a Curie-Weiss law with an effective moment

of $10.85 \pm .95 \mu_B$ and a paramagnetic Curie temperature of -3.55°K . The theoretical effective moment, obtained from the weighted average of these impurities, was $9.86 \mu_B$. Due to the range of values of the effective moments, resulting from the $\pm 20\%$ accuracy of the mass spectrographic analysis, it is impossible to say that enhancement has occurred. However it can be safely assumed that if enhancement of the effective moment has occurred it is not by more than 10 or 15%.

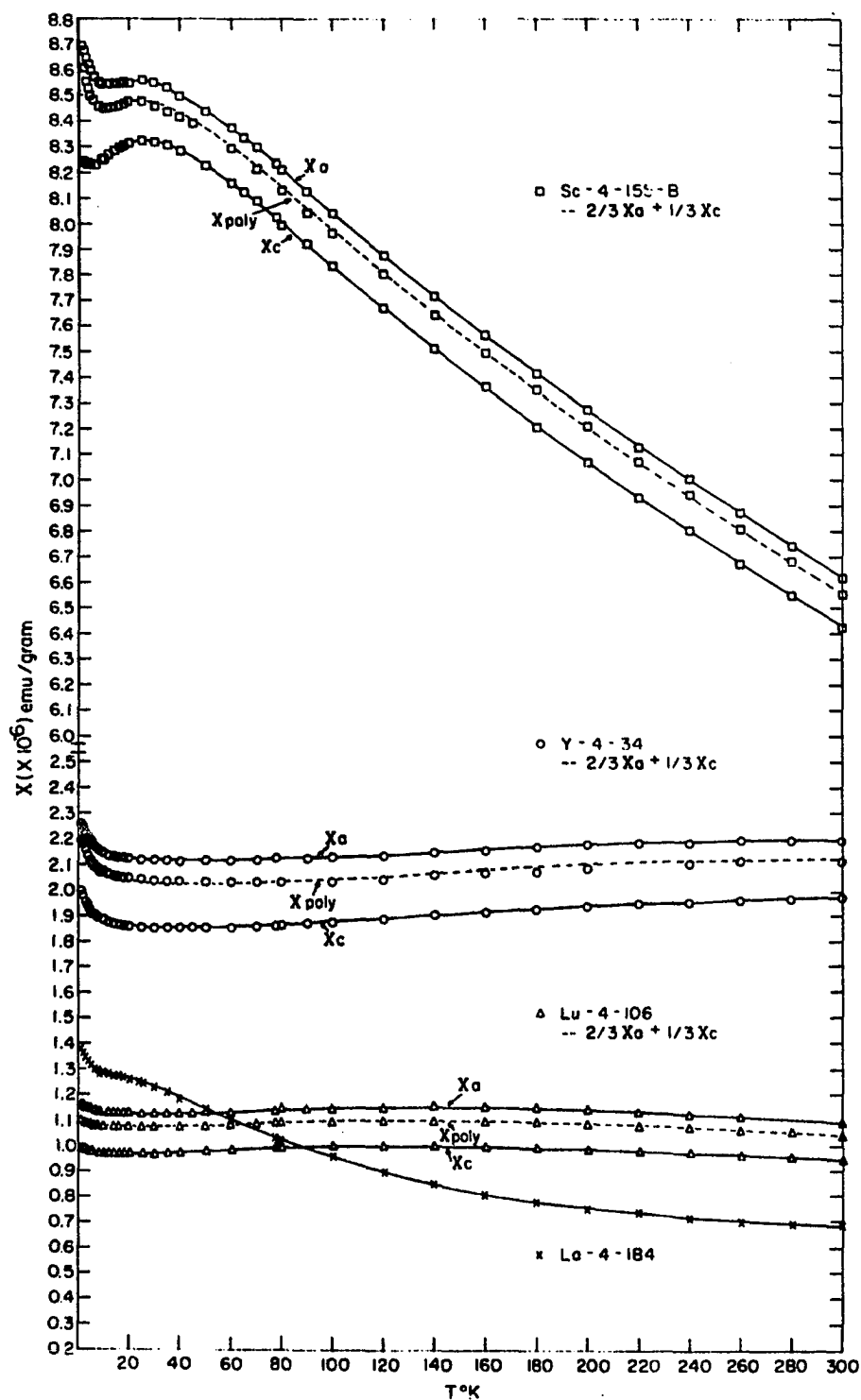


Fig. 41. Magnetic susceptibilities of scandium, yttrium, lanthanum and lutetium metal.

VI. DISCUSSION

A. Pure Metals

Because of the considerable discrepancies in past results, the magnetic susceptibilities of scandium, yttrium and lanthanum metals have been measured. The first temperature dependent measurements of both single and polycrystalline lutetium were also carried out. The metals used in this investigation are believed to be of significantly higher purity and more thoroughly characterized than those used in past studies. Since it was not clear how impurities effect the susceptibility, a number of alloys containing known amounts of various impurities was measured. These results go far in explaining the discrepancies in the previously reported results and tend to confirm the high purity of the samples measured in this study. These alloy results are discussed in Section VI.B.

Usually it has been the practice to regard the susceptibility of these metals as the sum of the following terms:

$$\chi_{\text{total}} = \chi_{\text{dia}}^{\text{core}} + \chi_{\text{dia}}^{\text{Landau}} + \chi_{\text{para}}^{\text{Pauli}} + \chi_{\text{para}}^{\text{orb}} \quad (5)$$

where $\chi_{\text{dia}}^{\text{core}}$ is the diamagnetism of the ion core, $\chi_{\text{dia}}^{\text{Landau}}$ is the diamagnetism of the conduction electrons, $\chi_{\text{para}}^{\text{Pauli}}$ is the Pauli spin paramagnetism of the conduction electrons and $\chi_{\text{para}}^{\text{orb}}$ is the orbital paramagnetism of the d band electrons. While the ultimate goal of an investigation of this type is to

determine the magnitude of these contributions, such a breakdown is extremely difficult at this time due to the lack of reliable quantitative predictions. Several investigators have recently attempted to separate these various contributions to the total susceptibility of scandium.^{4,15} However the considerable disagreement between their results attests to the difficulty of such a task. For this reason no attempt was made to partition the total susceptibility of these metals.

From the experimental results the following observations are noted:

(1) All of the single crystal specimens of scandium, yttrium and lutetium were found to have χ_a greater than χ_c . In the case of scandium this order agrees with those recently reported by Ross et al.¹⁵ but are in disagreement with those reported by Chechernikov et al.¹¹ and Wohlleben.¹² No reason can be given for this discrepancy.

(2) The room temperature magnetic anisotropy of the single crystals was found to vary from a high of roughly $.25 \times 10^{-6}$ emu/gram in yttrium to a low of $.15 \times 10^{-6}$ emu/gram in lutetium. Whereas the anisotropy of both of these metals was almost constant with temperature, the anisotropy in all of the scandium single crystals was observed to increase sharply below 30°K. Ross et al.¹⁵ observed similar anisotropic behavior in his scandium crystals but felt that the increase was due to some localized magnetic impurity effect. However the results of this study indicate that this is unlikely in light

of the small concentration of magnetic impurities believed present in these samples. Furthermore the contribution of small amounts of these magnetic impurities would not be expected to be significant until a temperature somewhat lower than 30°K.

(3) The relationship $\chi_{\text{poly}} = 2/3\chi_a + 1/3\chi_c$ was found to be quite well obeyed provided both specimens were prepared from the same batch of metal and did not contain inordinate amounts of impurities, especially iron. It was found necessary to recrystallize the polycrystalline samples to remove the considerable preferred orientation remaining in some of the samples. Otherwise the polycrystalline values could deviate considerably from the weighted average of the single crystal data. This was particularly true in the case of polycrystalline lutetium where anisotropies of over 40% of the single crystal values were observed in nonrecrystallized specimens. No recrystallization was found necessary for the polycrystalline scandium samples.

(4) As shown in Fig. 42, large differences were observed in $\chi(T)$ for these four metals. Whereas yttrium and lutetium are almost independent of temperature, the susceptibilities of scandium and lanthanum were found to have a significant negative temperature dependence. A previously unreported maximum was found at 30°K in scandium and a broad, though quite discernable maximum was found at 120°K in lutetium. Gardner and

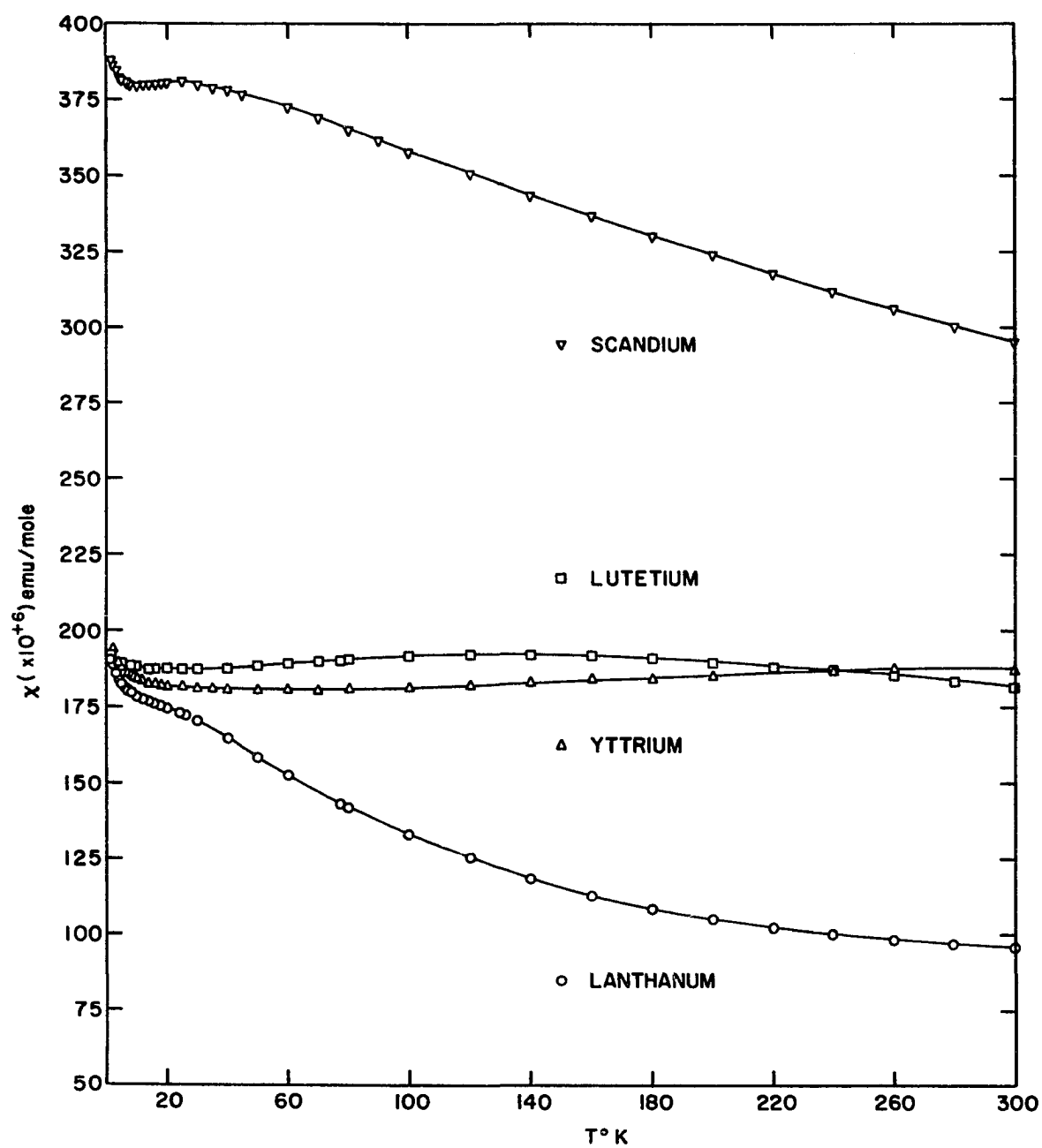


Fig. 42. The molar susceptibilities of polycrystalline scandium, yttrium, lanthanum and lutetium.

Penfold²¹ reported a similar maximum at 300°K in yttrium and speculated that it resulted from fine structure in the density of states curve, i.e., due to the temperature dependence of the Pauli spin paramagnetism. While it is possible to explain almost any $\chi(T)$ curve on the basis of a simple or collective electron band model,^{44,45} such an interpretation must await more accurate and detailed band calculations than those currently available.

(5) Of these four metals, scandium is the only one which clearly obeys a Curie-Weiss relationship. The effective moment of $1.647 \mu_B$ found for pure polycrystalline scandium is in fair agreement with the value of $1.67 \mu_B$ reported by Chechernikov et al.¹¹ However their value of -1050°K for θ is considerably larger than the value of -847°K found in this study. Their value is believed to reflect the presence of considerable gaseous impurities since it is close to the value of -1025°K found for a scandium -1.42 a/o oxygen alloy. Molybdenum may have also contributed to this discrepancy since their metal was prepared in a crucible of this material and was not distilled. However they reported only .002 w/o of this impurity which is difficult to explain in light of the relatively high solubility of refractory metals in scandium.

While the temperature dependence of scandium has usually been explained on the basis of a collective electron band model,^{4,15} the excellent Curie-Weiss behavior suggests that it may arise from an unpaired electron in a bound or highly

localized d state. The theoretical effective moment of a single bound d electron with full spin and orbital moment would be $1.55 \mu_B$ while that of a bound electron with spin only would be $1.73 \mu_B$. The effective moment of $1.647 \mu_B$ found in this study indicates that scandium may have either a partially localized d electron or, alternatively, a fully localized electron with a partially unquenched orbital angular moment. The existence of such a bound state has been proposed by Wohllleben.^{12,17} In light of this model, however, the decrease in the susceptibility at 30°K is difficult to understand unless the electron becomes increasingly delocalized as the temperature is lowered or there is antiferromagnetic ordering. The maximum in the susceptibility combined with the large negative paramagnetic Curie temperature suggests the possibility of the latter. On the other hand, if antiferromagnetic ordering occurred one would expect to find field dependence below 30°K. However none was observed above 2 or 3°K. Below these temperatures the field dependence is believed due to magnetic impurities. Furthermore no anomalies were observed in the electrical resistivity¹⁰ or specific heat⁴⁶ measurements in the neighborhood of 30°K.

(6) Lanthanum exhibited Curie-Weiss behavior between 30 and 160°K. Over this temperature range μ_{eff} and θ were found to be .580 and -216°K respectively. Above 160°K the slope of the Curie-Weiss plot decreased, suggesting that the moment may be larger at higher temperatures.

Although a number of investigators have reported measuring various physical properties of pure fcc lanthanum, it was found that this phase could not be stabilized at room temperature if the lanthanum was of high purity. Before pure fcc phase could be obtained it was found necessary to add over 1.0 a/o oxygen. Similar attempts to quench in the high temperature phase by adding almost 2.0 a/o hydrogen proved unsuccessful. Apparently the diffusion rate of hydrogen is too rapid to prevent the transformation. By measuring a lanthanum-1.66 a/o oxygen alloy in both fcc and dhcp and assuming that oxygen lowered the susceptibility by the same amount in both phases, an estimate of pure fcc lanthanum was made. This estimate found fcc lanthanum to have a susceptibility approximately 10% higher than dhcp lanthanum at room temperature but very nearly the same at low temperatures. It is felt that the somewhat higher values for dhcp lanthanum found at room temperature by both Lock²⁵ and Wohllleben¹² may be due to fcc phase in their samples.

B. Effects of Nonmagnetic Impurities

Previous magnetic susceptibility measurements of scandium metal show considerable scatter in both χ and its temperature dependence. These discrepancies apparently resulted from a combination of magnetic and nonmagnetic impurities in the various samples. Although magnetic rare earth impurities can completely dominate the susceptibility at low temperatures,

small amounts were found to increase χ only slightly above 100°K. In contrast nonmagnetic impurities, in concentrations conceivably present in these metals, were found to have a significant effect at both high and low temperatures. The fact that the room temperature susceptibilities of both scandium and yttrium are the highest reported is seen as indicating that the metals measured in this investigation contained fewer nonmagnetic impurities than that used in past studies. Further evidence of the high purity of the measured specimens is the smaller amount of upturn in the data at the lowest temperatures, indicating fewer paramagnetic impurities.

As expected, nonmagnetic impurities were found to effect the susceptibility differently depending on whether they were in solution or present as a second phase precipitate. Beyond the solubility limit of a particular impurity the susceptibility of the alloys appears to approach the values expected from the mole fractions of the impurities present, i.e., $\chi_{\text{alloy}} = N_R \chi_R + (N_R - 1) \chi_{\text{imp}}$. Here N_R is the mole fraction of the rare earth in the alloy. This equation would represent the susceptibility of a completely inhomogeneous mixture of the two constituents. One interesting result of this behavior is that the considerable scatter between the previous measurements on scandium can be directly attributed to the fact that nonmagnetic impurities, in particular oxygen and tantalum, have a higher solubility in scandium than in, for example, yttrium where better agreement was observed.

Due to this fairly high solubility of nonmagnetic impurities in scandium, a systematic study of their effect on its susceptibility was made. The following observations and trends were noted:

(1) The maximum at 30°K smoothed out and finally disappeared with increased solute concentration. The disappearance of this maximum upon the addition of relatively small amounts of both magnetic and nonmagnetic impurities is further indication of the high purity of the scandium starting material.

(2) Nonmetallic impurities such as oxygen and hydrogen lowered the susceptibility over the entire temperature range. Over the limited concentration range studied this decrease was found to be fairly linear with concentration but increased with decreasing temperature. The effective moment of the scandium ion was found to increase slightly with increased solute concentration. A considerable increase was observed in the paramagnetic Curie temperature.

(3) In general, nonmagnetic metallic impurities (Group IVB, Group VB and Th) were found to decrease the susceptibility at room temperature while either increasing or only slightly decreasing the susceptibility at low temperatures. The effect on the susceptibility was strongly dependent on the atomic weight of the solute and independent of its valence. A plot of the susceptibility at 300°K vs a/o solute for a series of scandium-titanium alloys showed a

bump at 3 a/o. A similar plot for the 10°K data revealed a sharp maximum at the same concentration. A discontinuity was also observed at 3 a/o in a series of scandium-tantalum alloys but its significance is in question due to the large amount of second phase in the alloy. No alloys were prepared beyond a concentration of 1.5 a/o in any of the other alloy systems. Provided the solubility limit has not been exceeded, both the effective moment and paramagnetic Curie temperature were found to decrease with increasing impurity concentration.

The effect of several nonmagnetic metallic impurities on the susceptibility of scandium has been previously reported.^{5,16,18} Although most of these results disagree considerably from those found in this study, all but Isaacs et al.¹⁶ reported a general decrease in the room temperature susceptibility upon alloying with both tetravalent (Group IVB and Th) and pentavalent (Group VB) metals. Two quite different explanations have been proposed to explain this decrease. One is based on the effect of alloying on the density of states and the Fermi level and the second on spin orbit scattering of the host conduction electrons by the solute atoms. This latter explanation was proposed by Wohllleben and Luo¹⁸ to explain the linearity which they observed between the decrease and the difference in the spectroscopic spin orbit energy ($\Delta\lambda$) between the host and the solute atoms. Much of their work was repeated using what is believed to be much purer starting

material. These results, and theirs, are shown in Fig. 43. As noted, good linearity was observed between the room temperature decrease and $\Delta\lambda$ in this study. However no difference was found between the effect of tetravalent and pentavalent impurities as they reported. Although the possible significance of this linearity can not be overlooked, it is felt that such a scattering mechanism does not adequately explain the experimental results because it can not explain the low temperature increase in the susceptibility observed in a number of the alloys, for example those containing titanium. Such a scattering mechanism would always result in a decrease in the susceptibility. Likewise it is difficult to explain the large decrease observed upon the addition of hydrogen and oxygen since both of these impurities would have a small spin orbit energy.^{47,48,49}

The more plausible explanation of the susceptibility change, particularly for the metallic impurities, is that the addition of solute shifts the Fermi energy of the host. Since E_f is believed to lie in the neighborhood of a peak in the density of states curve,⁵⁰ such a shift would result in a decrease in the density of states for both an increasing and decreasing e/a ratio. This decrease would reflect itself in a corresponding decrease in the Pauli spin paramagnetism. The low temperature increase in a number of the alloys and the discontinuity at 3.0 a/o in the scandium-titanium alloys probably results from fine structure in the density of states

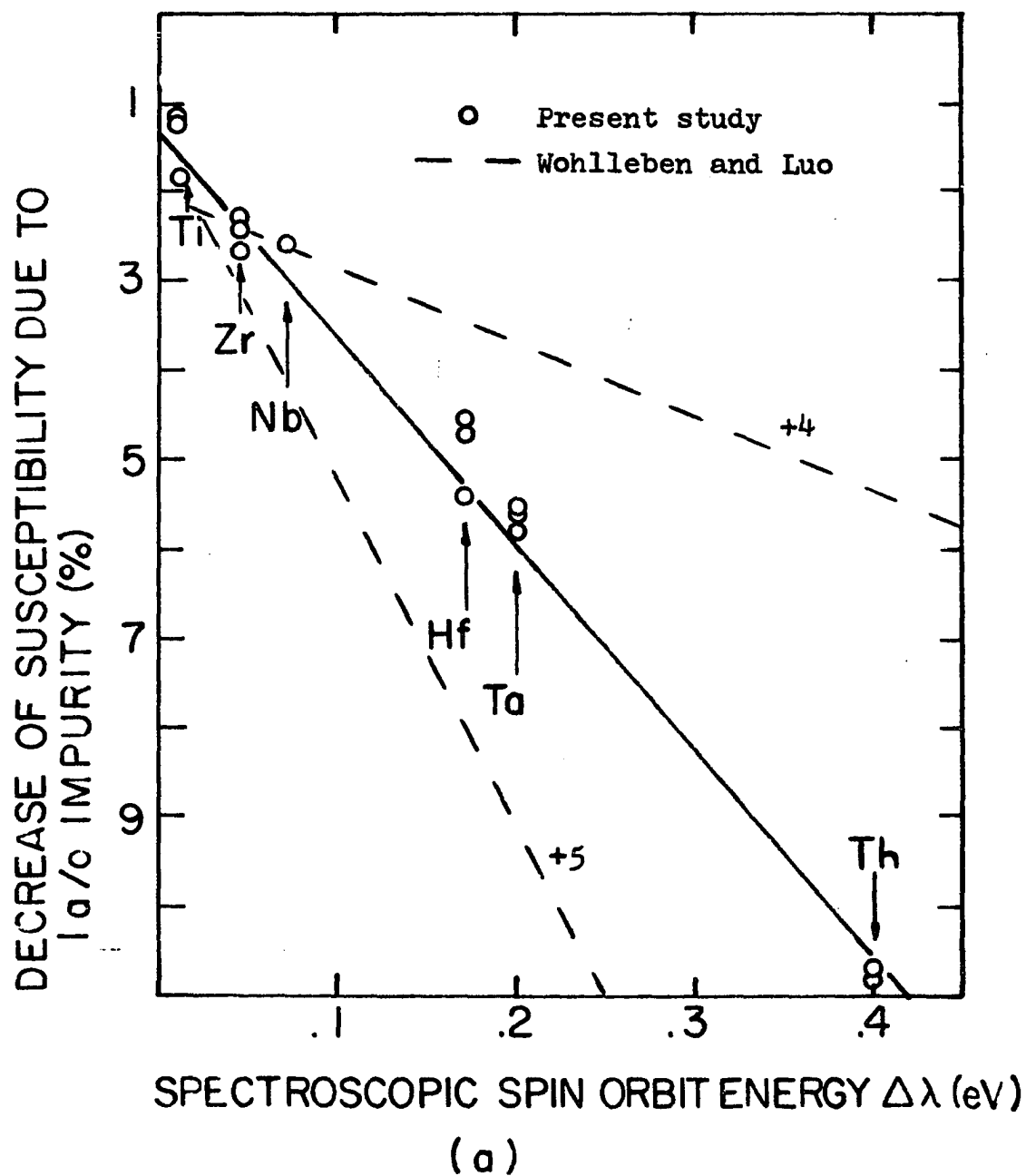


Fig. 43. The decrease in the susceptibility of scandium at 300°K for a number of metallic impurities versus the difference in the spectroscopic spin orbit energy between the host and solute atoms.

curves.

It is clear, however, that the frequently invoked rigid band model can not adequately explain the experimental results. This is so primarily because there is no relationship between the change in the susceptibility and the valence of the solute. As shown in Table IV the susceptibility at 300°K for alloys containing 1.0 a/o of the tetravalent impurities titanium, zirconium and hafnium was 1.18%, 2.41% and 5.32% respectively. The corresponding decrease for 1.0 a/o niobium and tantalum, reportedly pentavalent impurities, was 2.60% and 5.65% or very nearly the same as the values for zirconium and hafnium. A rough correction for the diamagnetism of the ion cores changed these values only slightly. Thus it is seen that the decrease is strongly dependent on the atomic weight of the solute and independent of its valence. This behavior indicates a breakdown in the rigid band model.

Recently Isaacs et al.¹⁶ reported that the addition of 0.2 a/o cerium and 0.5 a/o titanium increased the susceptibility of scandium while 2.0 a/o cerium decreased it. To explain this they proposed that the Fermi energy lie just to the left of a peak in the density of states curve. They speculated that the increased e/a ratio upon alloying would first increase and then decrease the density of states, resulting in a corresponding change in the Pauli spin paramagnetism. Their results, however, do not agree with those found in this study. As shown in Fig. 20 the addition of 0.5 a/o titanium was found to

decrease the susceptibility at room temperature and only slightly increase it at low temperatures. In no case did the addition of a nonmagnetic solute increase the room temperature susceptibility. No explanation can be given for this discrepancy except the possibility of some impurity effect. Iron would be the most likely possibility.

C. Behavior of Magnetic Impurities

In order to determine the behavior of dilute magnetic rare earth impurities in a scandium matrix, the susceptibilities of a series of scandium-gadolinium and scandium-erbium alloys were measured. After first subtracting off the susceptibility of pure scandium the values of μ_{eff} and θ were determined. The results were found to disagree considerably with those previously reported^{12,16} in which alloys of roughly the same concentration were measured. Both Isaacs et al.¹⁶ and Wohllleben¹² report that μ_{eff} of gadolinium and dysprosium are somewhat larger than the free ion values and increased with decreasing solute concentration. Both attributed this enhancement to a polarization of the scandium matrix by the magnetic moment of the solute ion. They also speculated that this polarization was long range in nature and that at dilute concentrations the individual solute atoms interact ferromagnetically.

In contrast to these results no appreciable enhancement of μ_{eff} was found in this study, even when the solute concen-

tration was significantly less than theirs. As shown in Tables VII and VIII, the effective moments of gadolinium and erbium were found to be independent of concentration, averaging $8.80 \mu_B$ and $10.08 \mu_B$. These values are roughly 10 and 6% larger than the free ion values. This enhancement is presumably due to the polarization of the conduction electrons. However the polarization is believed to be relatively short range in nature. The results of Wohleben¹² and Isaacs et al.¹⁶ are difficult to explain but impurity effects are considered most likely.

The paramagnetic Curie temperature for the erbium alloys, averaging -6.1°K , is attributed principally to crystal field splitting. Likewise the negative deviation from Curie-Weiss behavior at 8°K is believed due to this effect. At sufficiently low temperatures a population change occurs in the crystal field levels and therefore this deviation is expected. Gadolinium is known to also have a very small amount of crystal field splitting due to the Van Vleck mixing of higher states and this may be the source of a small part of the θ observed in the gadolinium alloys. However the field dependence observed in the samples at low temperatures suggests that it results from cooperative interaction involving exchange between the gadolinium atoms. The fact that both θ and the amount of field dependence increase with increasing gadolinium concentration supports this explanation.

D. Discussion of Error

From the scatter in repeated calibrations of the field gradient constants the absolute accuracy of the experimental data are estimated to be on the order of 1%. On the other hand, the relative accuracy is between .1 and .2%. These values are based on the results of measurements on the same sample at different stages of the investigation.

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