# PHYSICO-CHEMICAL PROPERTIES OF THE RARE-EARTH METALS, SCANDIUM, AND YTTRIUM

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LHE discovery of the special properties of rareearth metals-their superconductivity, ferromagnetism, large capture cross section for thermal neutrons, etc. and also the determination of their effective alloying action on many alloys-has excited ever increasing interest in the rare-earth metals. The rare-earth metals and the similar elements yttrium and scandium constitute one sixth of the periodic table. Whereas not so long ago they were a laboratory rarity, the situation has now changed radically. With the development of the production of titanium, niobium, tantalum and thorium there arose the problem of the rational utilization of the rare-earth metals present in the mineral raw material. A rare-earth industry is already in existence and is producing on an ever-increasing scale individual rare-earth metals, mixtures (Misch metal), and alloys with iron (ferrocerium) and other metals, as well as oxides and other rare-earth compounds. Rare-earth metals have become the object of laboratory investigation and plant work.<sup>[1]</sup> This in turn leads to increasing scientific research into their physico-chemical properties and to a search for new applications of the rare earths and their alloys.

The experimental data on the physico-chemical properties of the rare earths are being extended and refined as new methods of investigation, analysis, separation, and of the perfection of the technology of obtaining individual rare earths in pure form are being adopted. Initially the properties of the rare earths were determined from those of their compounds that were known at that time.

The main investigations of the physico-chemical constants of the rare-earth metals have been conducted during the past 15-20 years. Owing to the insufficient purity of the investigated metals, data on the physico-chemical constants of rare-earth metals available in the literature, even those on the melting and boiling points, and polymorphous transformations, are inexact and often contradictory.

Recent data on the properties of rare-earth metals using high-purity metals and more precise methods of investigation are beginning to appear in print systematically. In this article an attempt is made to generalize the material available in the literature, and specific experimental data on the chemical and physical properties of rare-earth metals obtained with 98-99% pure metals (the main impurities are other rare earths) are cited. <sup>[1,102,103,110]</sup>

# 1. ELECTRONIC STRUCTURE OF RARE-EARTH METALS

In the periodic table lanthanum and the 14 elements following it, from cerium (No. 58) and lutetium (No. 71), are referred to as rare-earth metals or lanthanides. Scandium (No. 21) and yttrium (No. 39) are also close to them in their properties.

As is well known, the chemical and certain physical properties of the elements are determined principally by the structure of their outer electron shells. The similarity of the properties of rare-earth metals is explained by the peculiarities of their electronic structure. With increasing nuclear charge (increasing atomic number) there is almost no change in the structure of the two outer electron shells (the O and P shells) of the lanthanide atoms, since the additional electrons fill the deeper-lying 4f level.

In the literature it is customary to divide the rareearth metals into two subgroups-the cerium subgroup (from cerium to gadolinium) and the yttrium subgroup (from terbium to lutetium). In some cases lanthanum is included in the cerium subgroup. However, lanthanum must not be considered a rare-earth metal, since it has no 4f electrons. In a number of works gadolinium is attributed to the yttrium subgroup. In general one must not draw a sharp dividing line between the cerium and yttrium subgroups, [2] since europium, gadolinium, and terbium can be included in different groups depending on the property considered. The physical basis for dividing the rareearth metals into two subgroups is the structure of the 4f electron shell, which can contain a maximum of fourteen electrons. However, without taking the electron spins into account it can contain only seven electrons. It is well known that as a rule a shell is stable when it is completely or half filled. Gadolinium has seven 4f electrons which all have, according to Hund's <sup>[3]</sup> rule, spins pointing in one direction, whereas in the following elements the 4f shell is filled with electrons having antiparallel spins.<sup>[3]</sup>

The small differences which exist between these elements are chiefly connected with effects due to differences in the dimensions of the atoms. The heavier the nucleus, the larger its positive charge. The increasing nuclear charge results in stronger attraction of the electrons, and this causes the shell to have a tendency to be pulled in. For this reason, the atoms of the heavy rare-earth metals have a smaller metallic radius, and are consequently more dense than the light rare-earth metals. Figure 1 shows the dependence of the change of the mean metallic radius of rare-earth atoms\* on the atomic number. Within the group of rare-earth metals from lanthanum to lutetium the mean metallic radius of the atoms decreases from 1.87 Å for lanthanum to 1.73 Å for lutetium. This phenomenon is referred to as the lanthanide contraction. Europium and ytterbium have maximum metallic radii and do not follow the general law.

In considering the influence of the electronic structure of the rare-earth metals on their physical properties, it is essential to note that the rare-earth metals belong to the elements of the transition group. The characteristic properties of transition-group metals are, as is well known, their high electrical resistance, high melting points, great strength and hardness; these are connected with the fact that not only the outer s electrons but also the more strongly bound electrons of inner shells take part in the interatomic bonding.

One characteristic of the transition metals is the closeness of the energy levels of a number of shells. With a change in temperature a transition of electrons from one state to another can thus take place easily. A change of the electron distribution in the solid state commonly leads to a change in the crystal structure. The polymorphism of a number of rare-earth metals is connected with this fact. The presence of an unfilled inner shell greatly influences the magnetic properties. The existence of uncompensated electron spins gives rise to large values of the magnetic susceptibility, and with the occurrence of the so-called exchange interaction, to ferromagnetism.

The whole above discussion of the electronic structure of rare-earth metals refers to isolated atoms. In real crystals of solids the energy states change sharply, and therefore the whole discussion for the isolated atoms can be transferred to the case of a real crystal only schematically.

#### 2. CHEMICAL PROPERTIES

The rare-earth metals are characterized by a considerable similarity of their chemical properties. As is well known, the chemical properties of an atom are chiefly determined by the outer-shell electrons. These electrons determine its valence, its ability to give up or take up electrons. The rare-earth metals exhibit a similarity of chemical properties because the electrons of the 4f level are screened from the common external interactions by the closed shells surrounding them, and exert almost no influence on the chemical activity of these elements. <sup>[4]</sup> The prop-



FIG. 1. The dependence of the mean metallic radius of atoms of rare-earth metals on their atomic number.

erties of the rare-earth metals depend almost exclusively on the configuration of the three outer electrons, and this configuration is identical for all of them; it is for this reason that almost all of them are commonly found to be trivalent, with the exception of europium and ytterbium which are divalent. The electronegativities of the rare-earth metals calculated according to Gordy [5] have almost the same value for the whole series (Fig. 2), since the electronegativity expresses in first approximation the bond energy between two elements. The anomalies for europium and ytterbium are in this case also connected with the transfer of 6s electrons only, since in the formula which determines the electronegativity,  $x = 0.31 \times$ (n' + 1)/r + 0.50, the quantity n' expressing the number of valence electrons enters in the numerator; r is the atomic radius. Europium and ytterbium are very similar in their physico-chemical properties to the alkaline-earth metals.

The fundamental chemical properties of the rareearth metals were predicted and determined by D. I. Mendeleev. He was the first to determine the specific heat of cerium and lanthanum. On the basis of the periodic law of the elements Mendeleev assumed the rare-earth metals to be trivalent and corrected the atomic weights of yttrium, lanthanum, cerium, and erbium, whose values turned out to be much too low.

The rare-earth metals possess considerable chemical activity. A fresh cut of a rare-earth metal differs little in its external form and luster from a cut of common iron. After prolonged exposure to air the rare-earth metals begin to be covered, some to a larger and some to a smaller extent, by a film of oxide. In the oxidation of cerium at room temperature there occurs the special phenomenon of pyrophoricity —the production of sparks on being scratched or struck. Lanthanum and cerium are most strongly



FIG. 2. The dependence of the electronegativity of rare-earth metals on their atomic number.

<sup>\*</sup>The metallic radius is calculated from the lattice parameters of the pure metal.

oxidized in air. The elements belonging to the yttrium subgroup are considerably more stable with respect to air than the elements of the cerium subgroup. With increasing atomic number, a certain increase in the chemical stability of the rare-earth metals is observed. The last of them, lutetium, is close in its chemical stability to the platinum metals. Metallic scandium is less subject to oxidation than the rareearth metals.

Being chemically very active, the rare-earth metals readily interact with many elements. Many of their compounds are formed with considerable evolution of heat; the rare-earth metals exceed almost all other elements in the heat they evolve in the formation of compounds.

At room temperature cerium, lanthanum, neodymium, praseodymium, gadolinium and others react slowly with hydrogen; <sup>[6]</sup> with increasing temperature the rate of the reaction increases. The rare-earth metals form hydrides of the type  $RH_2$  and  $RH_3$  where R denotes the rare-earth metal. The rare-earth metals react intensively with the halogens, the activity of the reaction decreasing in the following order: fluorine—chlorine—bromine—iodine. On being heated to red heat with nitrogen, they form nitrides with the general formula RN. Carbon forms with the rare-earth metals carbides with a general formula  $C_2R$ . The formation of carbides of the rare-earth metals generally occurs at the melting point.

The rare-earths sulfides have a general formula  $R_2S_3$  and are produced indirectly, for instance under the action of hydrogen sulfide on the chlorides. The sulfides are high melting and stable in the presence of numerous molten metals.

The most interesting and important compounds of the rare-earth elements are their oxides.

The rare-earth oxides are extremely high-melting powders. They possess a sharply pronounced funda-

Table I.	Crystal	structure	and	lattice	parameters	of the	rare-
		earth	elen	$nents.^{ll}$	9J		

	Purity,	Modifi-	Structure	Lattice g	parameters	
Element	%	cation	type	<i>a</i> , Å	c, Å	Remarks
Lantha- num	99,8	α-La β-La γ-La	hcp fcc bcc	$\begin{array}{r} 3,770 \pm 0,002 \\ 5.304 \pm 0,003 \\ 4.26 \pm 0,01 \end{array}$	$12,159 \pm 0.008$	$\beta$ -La is ob- served when the metal is obtained by electrolysis
Cerium	99,9	α-Ce β-Ce γ-Ce δ-Ce	fcc hcp fcc bcc	$\begin{array}{r} 4.85 \pm 0.01 \\ 3.68 \\ 5.1612 \pm 0.0005 \\ 4.11 \pm 0.01 \end{array}$	11.92	
Praseo- dymium	99,9	α-Pr β-Pr	hcp bcc	$3.6725 \pm 0.0007$ $4,13 \pm 0.01$	<b>11,8354±0.0012</b>	
Neody- mium	99.8	α-Nd β-Nd	hcp bcc	${3,6579 \pm 0,0003 \atop 4,13 \pm 0,01}$	$11.7992 \pm 0.0005$	
Samarium	99	α-Sm β-Sm	hombohedr bcc	al 8,966 4,07	a=23°13′	The param- eters of the hexag- onal lat-
Europium	98—99		bcc	$4,5820 \pm 0.0004$		tice are: a=3,621 $\pm 0.007$ c=26.25 $\pm 0.005$
Gado- linium	99.7	α-Gd β-Gd	hcp bcc	$3.6360 \pm 0.0009$ 4.06	$5,7826 \pm 0.0006$	
Terbium	99,9	α-Tb	hcp	$3,6010 \pm 0,0003$	$5.6936 \pm 0.0002$	
Dyspro- sium	99,8		hcp	$3.5903 \pm 0,0001$	$5,6475 \pm 0.0002$	
Holmium	99.4		hcp	$3.5773 \pm 0,0001$	5,6158 ± 0,0002	
Erbium	99.8		hcp	$3.5588 \pm 0,0003$	$5,5874 \pm 0.0002$	
Thulium	99.9		hcp	$3,5375 \pm 0,0001$	$5.5546 \pm 0.0004$	
Ytter- bium	99,9	α-Υb β-Υb	fcc bcc	$5.4862 \pm 0,0004$ 4,45	-	ļ
Lutetium	99,9		hcp	$3.5031 \pm 0,0004$	$5.5509 \pm 0.0004$	
Scandium	99.6		hcp	3.3090 ± 0,0001	5.2733±0,0016	
Yttrium	99.4	α-Υ β-Υ	hcp bcc	$\begin{vmatrix} 3,6474 \pm 0,0007 \\ 4,11 \pm 0.02 \end{vmatrix}$	$5,7306 \pm 0.0008$	

mental character which weakens on going from lanthanum to lutetium. The solubility of the  $R_2O_3$  type of oxides in acids decreases with increasing atomic number. The oxides are insoluble in water; they can, however, combine with it to form hydroxides. The rare-earth hydroxides are usually obtained indirectly, by adding bases to solutions of rare-earth salts.

All rare earths are rather unstable against acids. Sulfuric and hydrochloric acids of arbitrary concentration, and also concentrated nitric acid dissolve the rare earths: dilute nitric acid acts only on cerium.<sup>[7]</sup>

The rare earths are rather inert to bases. They have the ability to extract the hydrogen from water, acting as powerful reducing agents. They form a large number of salts both with inorganic and organic anions. Their halides, nitrites, sulfates, oxylates, as well as their binary salts are characterized by differing solubilities, a fact utilized for the separation of the rare earths from each other.<sup>[8]</sup>

#### 3. PHYSICAL PROPERTIES

<u>Crystal structure</u>. Almost all rare earths (with the exception of cerium, europium, and ytterbium), as well as scandium and yttrium, have at room temperature hexagonal close-packed structures. Data on the crystal structures and lattice parameters of the rare earths are listed in Table I.

K. Gschneidner <sup>[3]</sup> reports on the basis of a survey of a large number of works on the crystal structures of the rare-earth elements that there exist three different forms of close-packed hexagonal structures (Fig. 3). These differ from each other in the order of the layers in the unit cells and in the c/a ratio. The majority of the rare-earths have hexagonal closepacked lattices of the common type with a c/a ratio of about 1.6 (Fig. 3a). Lanthanum, praseodymium, and neodymium have hexagonal structures of the lanthanum type (Fig. 3b) with a c/a ratio of 3.2, i.e. twice as large as that of the common hexagonal metals. Samarium has an unusual structure caused by the peculiar arrangement of the layers in the crystal lattice; if the unit cell is assumed hexagonal, then the c axis is found to be 4.5 times larger than its normal value (Fig. 3c). The true structure of samarium is rhombohedral.<sup>[10]</sup> Europium crystallizes in a body-centered <sup>[11]</sup> and ytterbium in a face-centered cubic structure.<sup>[12]</sup> The crystal structure of promethium is unknown.

The accuracy of the lattice parameters is affected considerably by the purity of the metals. In view of the fact that up to the present the rare-earth metals have not been obtained in a pure state, the data on their crystal structures and lattice parameters will in the future be refined. It can be seen from Table I that in the hexagonal rare-earth metals the lattice parameters decrease with increasing atomic number.

<u>The density of rare-earth metals</u>. The densities of the rare-earth metals have been determined by two methods: the theoretical value of the density was calculated from the x-ray diffraction data, and the actual value of the density was determined by the pycnometer method or by hydrostatic weighing.<sup>[13]</sup> The obtained data on the density are presented in Table II.

The cited data have been used to plot the dependence of the density on the atomic number of the element (Fig. 4). The densities of the majority of the rare earths increase monotonically with increasing atomic number in accordance with the lanthanide contraction, and fall well on an additive straight line.

Table II. The densities of the rare-earth metals

Element	Calcu- lated density, g/cm <sup>3</sup>	Actual den- sity, g/cm <sup>3</sup>	Element	Calcu- lated density, g/cm <sup>3</sup>	Actual den- sity, g/cm <sup>3</sup>
Lanth anum Cerium Praseodymium Neodymium Samarium Europium Gadolinium Terbium	$\begin{array}{c} 6.162 \\ 6.768 \\ 6.769 \\ 7.007 \\ 7.536 \\ 5.166 \\ 7.868 \\ 8.253 \end{array}$	$\begin{array}{c} 6.18\\ 6.79\\ 6.71\\ 6.96\\ 7.50\\ 5.30\\ 7.80\\ 8.19 \end{array}$	Dysprosium Holmium Erbium Thulium Ytterbium Lutetium Scandium Yttrium	$\begin{array}{c} 8,565\\ 8,799\\ 9,058\\ 9,318\\ 6.959\\ 9,849\\ 2.995\\ 4.472\end{array}$	$\begin{array}{c} 8,35\\ 8,65\\ 9,01\\ 9,20\\ 7,02\\ 9,79\\ 2,90\\ 4,50\end{array}$



FIG. 3. Different forms of the hexagonal closepacked structures of rare-earth metals. a) Normal hexagonal structure of the Mg A3 type; b) La A3 type hexagonal structure with a doubled c axis; c) hexagonal samarium-type structure.



FIG. 4. The dependence of the density of the rare-earth metals on the atomic number.

The lowest values of the density are those of europium and ytterbium, as well as those of scandium and yttrium. The density of the rare earths varies from 6.18 (lanthanum) to 9.85 (lutetium) g/cm<sup>3</sup>. Many rare earths are close in their specific weight to iron and steel. Scandium and yttrium belong, as far as their specific weight is concerned, to the same series as aluminum, beryllium, and titanium.

Melting points and temperatures of polymorhous transformations of the rare-earth metals. To determine the melting points of the rare earths, two methods are mainly employed: the determination of the setting in of melting with the aid of an optical pyrometer with a disappearing filament, <sup>[14]</sup> and the method of differential thermal analysis.<sup>[15]</sup>

Differential thermal analysis requires the use of tantalum crucibles and covers for the thermocouples,



FIG. 5. The dependence of the melting point of the rare-earth metals on the atomic number.

heating in vacuum or in an inert gas, high-temperature thermocouples, and furnaces enabling one to attain temperatures of 1600-1700°C.

Table III lists the melting points and the polymorphous transformations of the rare earths obtained from thermal analysis.

The dependence of the melting points of the rareearth metals on their atomic number is shown graphically in Fig. 5. An almost linear dependence of the melting points on the atomic number is observed for the cerium and yttrium subgroups. Europium and ytterbium, having the lowest melting points, are exceptions.

According to the most recent data <sup>[16]</sup> the following metals are polymorphous: lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, terbium, ytterbium, scandium, and yttrium. All known

Element	Melting point, °C	Latent heat of melting ∆H, kcal/mole	Temperature of polymor- phous transition, °C	Heat of poly- morphous transition ΔH, kcal/mole
Lanthanum	$920\pm5$	1,6	$\begin{array}{c} \alpha \rightarrow \beta & 310 \pm 5 \\ (\beta \rightarrow \alpha & 220 \pm 20) \end{array}$	0,095
			$\beta \rightarrow \gamma 864$	0,76
Cerium	$797\pm3$	$1.238 \pm 0.004$	$\alpha \rightarrow \gamma - 113 \pm 5$ $\gamma \rightarrow \alpha - 178 \pm 5$	$0.88 \pm 0.04$
			$ \begin{array}{c} \beta \rightarrow \gamma & 100 \pm 5 \\ \gamma \rightarrow \beta - 10 \pm 5 \\ \gamma \rightarrow \delta & 725 \end{array} $	$0.065 \\ 0.700 \pm 0.008$
Praseodymium	935 <u>+</u> 5	1.650	$\alpha \rightarrow \beta$ 792	0.760
Neodymium	$1024 \pm 5$	1.705 ± 0,019	$\alpha \rightarrow \beta  862$	$0,713 \pm 0.015$
Samarium	$1072\pm5$	$2,061\pm0,015$	$\alpha \rightarrow \beta$ 917	$0.744 \pm 0.036$
Europium	$826\pm10$	2.0	none	—
Gadolinium	$1312\pm5$	2,1	$\alpha \rightarrow \beta$ 1264	1,03
Terbium	$1364\pm5$	2.2	$\alpha \rightarrow \beta$ 1326	1,06
Dysprosium	$1407\pm5$	3.8	—	-
Holmium	$1461\pm5$	4.1	—	-
Erbium	$1497\pm5$	4.1	-	—
Thulium	$1545\pm5$	4.3	—	—
Ytterbium	$824\pm5$	1,800	$\alpha \rightarrow \beta$ 798	0,425
Lutetium	$1652 \pm 5$	4,5		—
Scandium	$1530\pm5$	4.2	$\alpha \rightarrow \beta$ 1450	—
Yttrium	$1502\pm7$	2.4	$1490\pm5$	1,18
				ł

Table III. Melting points, heats of fusion, temperatures and heats of polymorphous transformations of rare-earth metals<sup>[11,29-33]</sup>

high-temperature modifications of the rare-earth metals are body-centered cubic. Recently it has been found that dysprosium, holmium, and lutetium have polymorphous transformations at  $1390 \pm 10^{\circ}$ ,  $1440 \pm 10^{\circ}$ , and  $1340 \pm 10^{\circ}$ C respectively.<sup>[17]</sup> In analogy with other rare earths and with a previously established rule <sup>[102]</sup> that the high-temperature modification of a polymorphous metal must possess maximum plasticity, it can be presumed that the high-temperature determine the forms of these metals must be body-centered cubic.

Cerium has interesting polymorphous transformations; it has four modifications:  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ .<sup>[18]</sup> On cooling cerium having the room-temperature crystal structure  $\gamma$ -Ce (face-centered cubic,  $a = 5.1612 \pm 0.0005 \text{ Å}$ ) there begins at  $263 \pm 5^{\circ}$ K  $(-10 \pm 5^{\circ}C)$  to appear the  $\beta$ -Ce modification (hexagonal close packed, isomorphous with  $\alpha$ -La). This process of the production of  $\beta$ -Ce takes place down to  $95 \pm 5^{\circ}$ K (-178  $\pm 5^{\circ}$ C), at which temperature there begins, simultaneously with the production of  $\beta$ -Ce, the production of  $\alpha$ -Ce from  $\gamma$ -Ce.  $\alpha$ -Ce has also, like  $\gamma$ -Ce a face-centered cubic lattice, but with a smaller lattice parameter a = 4.85 Å. In this  $\gamma \rightarrow \alpha$ transformation there occurs a volume decrease by 16.5%. Obviously this is due to the transition of a 4f electron to the valence, probably the 5d, shell.

Depending on the rate of cooling, the presence of impurities, and the preliminary treatment of the initial cerium samples at helium temperature, there exists a variable-composition mixture of the  $\alpha$  and  $\beta$  modifications. Obviously, it is possible by varying the rate of cooling and the preliminary treatment of the samples to obtain only  $\alpha$ -Ce.

The temperatures at which the polymorphous transformations occur on heating metallic cerium above helium temperature differ from the corresponding temperatures observed on cooling. The  $\alpha \rightarrow \beta$  transformation begins at 125°K (-148°C) and termi-

nates at 200°K ( $-73^{\circ}$ C); the  $\alpha \rightarrow \gamma$  transformation begins at 160 ± 10°K ( $-113 \pm 10^{\circ}$ C) and terminates at 195 ± 15°K ( $-78 \pm 15^{\circ}$ C), and the  $\beta \rightarrow \gamma$  transformation begins at 373 ± 5°K ( $+100 \pm 5^{\circ}$ C) and terminates at 425 ± 5°K ( $152 \pm 5^{\circ}$ C). On further heating  $\gamma$ -Ce transforms at 725°C into  $\delta$ -Ce (body-centered cubic). A considerable number of papers has been devoted to the problem of the polymorphous transformations of cerium, and a more detailed description can be found in these works.<sup>[19-28]</sup>

Vapor pressure, boiling point, and heat of vaporization of the rare-earth metals. The methods for the determination of the vapor pressure, the boiling point, and the heat of vaporization of the rare-earth metals are described in detail in reference 34. The obtained experimental data are presented in Table IV.

Analyzing the data on the vapor pressure of the rare earths, it can be noted that the most volatile are ytterbium, europium, samarium, and thulium. The least volatile are lanthanum and cerium. The lowest boiling point is that of ytterbium, the highest that of lanthanum and cerium. There is no definite dependence of the boiling point on the atomic number of the metal. Only a certain general tendency towards lower boiling points with increasing atomic number is noted in the cerium subgroup.

<u>Thermal expansion</u>. The coefficients of thermal expansion were determined from dilatometric measurements and from x-ray investigations. The measurements were conducted in the temperature interval from -200 to 1000°C. The fundamental investigations were carried out by Trombe and Foex,  $^{[39-41]}$  Barson, Legvold and Spedding,  $^{[42]}$  and Savitskiĭ and Dashkovskiĭ.  $^{[43]}$  The mean coefficients of thermal expansion of rare-earth metals are given in Table V.

The general rules of the increase of the thermal expansion coefficient with increasing temperature are determined from the data. Europium is exceptional in that its coefficient of thermal expansion decreases

Element	Vapo log p (mm	r pressure, Hg) = $-A/T + B$	Heat of va- porization ∆Hyap	Temperature range of measure-	Boil- ing point,
	А	В	kcal/mole	ments, • C	۰C
Lanthanum Cerium	$20511 \pm 203$ $20304 \pm 81$	$8,364 \pm 0.113$ $8.306 \pm 0.045$	$93.8 \pm 0.9 \\ 92.9 \pm 0.4$	$\begin{array}{r} 1367 - 1744 \\ 1338 - 1765 \end{array}$	3470 3470
Praseodymium Neodymium Samarium	$17188 \pm 243$ 15450 	$8.098 \pm 0.156$ 7,32	$\begin{array}{c} 79.5 \pm 1.1 \\ 70.6 \pm 2.0 \\ 48.6 \pm 0.8 \end{array}$	$1150-1420 \\ 1075 \\ 538$	3017 3210 1670
Europium Gadolinium	$8982 \pm 16$	$8.160 \pm 0.027$	$\begin{array}{c c}41.1 \pm 0.1 \\77.5 \pm 3.1\end{array}$	460630 1275	1430 2830
Dysprosium Holmium	14920	8.62	$68.2 \pm 0.9$	542	2480 2330 2490
Erbium Thulium Vite 1	$14146 \pm 469 \\ 12552 \pm 45$	$6.625 \pm 0.315 \\ 9.176 \pm 0.046$	$64.7 \pm 2.5$ $57.4 \pm 0.2$ $20.5 \pm 4.4$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	2390 1720
Lutetium Scandium	17180	8.298	$59.5 \pm 1.1$ 78.6 + 0.7	1232-1475	1320 3000 2730
Yttrium	17500	8.91	80	13601600	2630

**Table IV.** Vapor pressure, boiling point, and the heat of vaporization of rare-earth metals <sup>[11,34,36-38]</sup>

with increasing temperature. It has been noted that the lighter rare-earth elements (lanthanum, cerium, praseodymium, and neodymium) have lower values of the thermal expansion coefficient than those belonging to the yttrium subgroup, as well as samarium and yttrium. Europium and ytterbium have higher values, approaching those of the alkaline-earth metals. X-ray investigations <sup>[44]</sup> at temperatures up to 850°C showed that, as a rule, the expansion of metals with a hexagonal structure takes place non-uniformly. The coefficient of thermal expansion along the c axis is twice as large as that along the a axis. For all polymorphous metals, lanthanum, cerium, praseodymium, and neodymium, there occurs a sharp reduction in the coefficient of expansion at the polymorphous transformation temperatures. For gadolinium and dysprosium an interesting peculiarity is observed at temperatures of the magnetic transformation (below the Curie point). namely there is almost no expansion along the c axis. For gadolinium, dysprosium, and terbium the coefficient of thermal expansion near the Curie points is negative. The majority of impurities in the rareearth metals give rise to an increase in the thermal expansion coefficient.<sup>[18]</sup>

Electrical properties of the rare-earth metals. The electrical properties of the rare earths have been studied by numerous authors.<sup>[45,48]</sup> The investigations were carried out at temperatures from 0.08 to 1163°K at normal and high pressures. There are no good conductors of electricity among the rare-earths (Table VI).

The resistivity of the rare earths is 40-70 times as large as that of copper and 25-50 times that of aluminum. Ytterbium has the lowest resistivity at

Table	v.	Thermal expansion coefficients	of
	ra	re-earth metals $[13, 17, 39-44]$ .	

	Expansion of	coefficient		
Element	At 25° 10 <sup>6</sup> (°C)-1	Me an value 10 <sup>6</sup> (°C) <sup>-1</sup>	Temperature interval, ° C	
a-Lanthanum $\beta$ -Lanthanum Cerium Praseodymium Neodymium Europium Gadolinium Terbium Dysprosium Holmium Erbium Thulium Ytterbium Lutetium Scandium Yttrium	$\begin{array}{c} 4.9 \pm 0.1 \\ \hline 8.5 \\ 4.8 \pm 0.6 \\ 6.7 \pm 0.4 \\ \hline 32.0 \\ 6.4 \pm 0.3 \\ 7.0 \pm 0.3 \\ 7.0 \pm 0.3 \\ 8.6 \pm 0.9 \\ 9.5 \\ 9.2 \pm 0.3 \\ 11.6 \\ 25.0 \\ 12.5 \\ 11.4 \\ 10.8 \end{array}$	$ \begin{bmatrix} 5.2 \\ 9.6 \\ 7.1 \\ 6.5 \\ 8.6 \\ 26 \pm 4 \\ 9.7 \\ 11.8 \\ 10.2 \\ 12.0 \\ 12.4 \\ 29.9 \\ 12.7 \\ 12.0 \\ 1$	$ \begin{array}{c} {\rm from}-173 \ {\rm to} \ +\\ +325 \ +\\ -173 \ +\\ -25 \ +\\ -173 \ +\\ -200 \ +\\ +25 \ +\\ -20 \ +\\ +\\ +20 \ +\\ +20 \ +\\ +\\ +20 \ +\\ +\\ +20 \ +\\ +\\ +20 \ +\\ +\\ +\\ +20 \ +\\ +\\ +\\ +\\ +\\ +20 \ +\\ +\\ +\\ +\\ +\\ +\\ +\\ +\\ +\\ +\\ +\\ +\\ +\\ $	310 775 725 800 350 780 950 950 950 853 700 956 1009 397

room temperature, while gadolinium has the highest. No correlation could be established between the resistivity and the atomic number of the rare earths. One can merely note that the resistivity of the yttriumsubgroup metals is slightly higher than that of the cerium subgroup.

The investigation of the temperature dependence of the resistivity made it possible to observe certain peculiar properties of the rare earths: the superconductivity of lanthanum, anomalies in the conductivity of cerium in the transition region, peculiarities in the conductivity of the elements of the yttrium group (gadolinium, terbium, dysprosium, etc.), which exhibit ferromagnetic properties. The increase of the resistance with increasing temperature common in metals is also observed for the rare-earth elements.

Element	Resistivity	Temper- ature, °C	Temperature coefficient of the resis- tivity $\alpha$ , $10^3 \times (^{\circ}C)^{-1}$	Remarks
a-Lanthanum β-Lanthanum γ-Lanthanum α-Cerium γ-Cerium α-Praseodymium β-Praseodymium β-Neodymium α-Samarium Europium	$56.8 \\ 96 \\ 126 \\ 34 \\ 75.3 \\ 68.0 \\ 132 \\ 64.3 \\ 137 \\ 88 \\ 81.3$	$25 \\ 560 \\ 890 \\ -249 \\ 25 \\ 770 \\ 25 \\ 820 \\ 25 \\ 890 \\ 25 \\ 25 \\ 25 \\ 25 \\ 25 \\ 25 \\ 25 \\ 2$	$ \begin{array}{c} 2.18 \\ - \\ 0.87 \\ - \\ 1.71 \\ 1.64 \\ 1.48 \\ 4.80 \\ \end{array} $	The value of $a$
a-Gadolinium a-Terbium Dysprosium Holmium Erbium Thulium a-Ytterbium Lutetium a-Scandium a-Yttrium	$\begin{array}{c} 140.5\\ 135.5\\ 56\\ 87\\ 107\\ 79\\ 27.0\\ 79\\ 66.3\\ 64.9\\ \end{array}$	25 18 25 25 25 25 25 25 25 26 25	1.76 0.91 1.19 1.71 2.01 1.95 1.30 1.4 —	The value of α was taken at 25°C

**Table VI.** Resistivity of rare-earth metals and its temperature coefficient.<sup>[13,17]</sup>

The superconductivity of the rare-earth metals has attracted considerable attention. Of all the rare earths, the superconductivity has been observed and studied only in lanthanum.<sup>[49-55]</sup> At low temperatures lanthanum has two modifications,  $\alpha$  and  $\beta$ . The mean temperatures of the  $\alpha$ -La and  $\beta$ -La transitions to the superconducting state are, according to the data of various investigators,  $4.90 \pm 0.10^{\circ}$ K for  $\alpha$ -La and  $5.85 \pm 0.11^{\circ}$ K for  $\beta$ -La.

The rare-earth metals from cerium to thulium are not superconductors on account of the spins of the unpaired 4f electrons.<sup>[56-58]</sup> It has been established experimentally that ytterbium does not become a superconductor down to  $1_{\bullet}24^{\circ}$ K. Data for europium are unavailable. The absence of superconductivity in scandium, yttrium, and lutetium is explained by some authors by the difference in the crystal structures of these metals and lanthanum. In investigations of the effect of pressure on the resistance, an anomalous variation of the resistance has been observed in many rare earths, with the exception of samarium.<sup>[60-61]</sup>

In cerium there occurs a strong change in the resistance which is connected with its low-temperature polymorphism. Ytterbium, on the other hand, is distinguished by a high resistance coefficient with a change in the pressure, and Bridgman assumes that at high temperatures it may undergo a polymorphous transformation, similar to the  $\gamma \rightarrow \alpha$  transformation in cerium.

Chemical compounds of rare-earth elements with the precious metals, as well as with germanium and silicon, possess very interesting electrical properties: they are superconductors at low temperatures; <sup>[62]</sup> the transition temperatures of these compounds are given in Table VII.

The selenides and tellurides of certain rare-earth metals (for example, gadolinium selenide) have semiconductor properties.<sup>[63]</sup>

According to the data in the literature, the hexaborides of the rare earths, in particular lanthanum hexaboride, have recently found application as materials for the preparation of cathodes of electron guns

**Table VII.** Temperatures of transitions to the superconducting state of some rare-earth compounds.

Compound	Transition temperature, • K	Compound	Transition temperature, • K
Sala	1.02	L u Oa	2.40
Scir <sub>2</sub>	1.03	LuOs <sub>2</sub>	5.49
Y Ir <sub>2</sub>	2.18	ScGe <sub>2</sub>	1,30-1.31
$YPt_2$	1.57	$YGe_2$	3.8
LaRu <sub>2</sub>	1.63	LaGe <sub>2</sub>	1.49
LaOs <sub>2</sub>	6.5	ScSi <sub>2</sub>	1
CeRů2	4,9	YSi <sub>2</sub>	1
ScRu <sub>2</sub>	1,67	LaSi <sub>2</sub>	1
ScOs <sub>2</sub>	4.6	CeSi <sub>2</sub>	1
YRu <sub>2</sub>	1,52	NdSi2	1
YOs,	4.7		1

of powerful electronic devices.<sup>[64]</sup> The advantage of these materials lies in their comparatively low work function, in the possibility of obtaining a high-density emission current, in the absence of cathode deterioration in air, in their ability to operate in low vacuum (up to  $10^{-2}$  mm Hg), and in their stability under ion bombardment.

The low value of the work function and the field emission are commonly explained by the pressure in the rare-earth hexaborides of free electrons, comparatively weakly bound to the metal and boron atoms.

The only disadvantage of the hexaborides appears to be their low resistivity. However, recently cathodes have been produced using solid solutions containing hexaborides with larger resistivities, the work function remaining unchanged.

Specific heat and thermal conductivity of rareearth metals. Many papers have been published on the specific heat of the rare earths. Worthy of special attention are the papers of Spedding and Gschneidner [13,48,65,66] who studied the majority of the rare earths. Lanthanum,<sup>[67]</sup> cerium,<sup>[68]</sup> praseodymium, neodymium, <sup>[29]</sup> ytterbium,<sup>[13]</sup> samarium,<sup>[54,29,65,69]</sup> gadolinium <sup>[70,71]</sup> terbium,<sup>[71,72,73]</sup> dysprosium, holmium, erbium,<sup>[74,75]</sup> scandium <sup>[76]</sup> have also been studied by other authors.

Of particular interest is the consideration of the effect of structural, magnetic, and electronic transitions on the temperature dependence of the specific heat. The majority of the rare-earth metals have, therefore, been investigated within a wide temperature range: from liquid helium temperature  $(4.2^{\circ}K)$  to their melting points. Almost all rare earths have been investigated at low temperatures. In many rare earths anomalies in the temperature dependence of



FIG. 6. The temperature dependence of the specific heat of rare-earth metals.

the specific heat have been noted (Fig. 6). Such an anomaly is, for example, observed at the temperature at which lanthanum goes over to the superconducting state. In the case of cerium points of inflection are observed in the temperature dependence of the specific heat which are connected with the low-temperature polymorphous transformations. The effect of magnetic transitions on the specific heat of the rare earths is clearly seen from the examples of gadolinium, terbium, dysprosium, holmium, and erbium. All magnetic transitions in these metals give rise to inflection points on the curves of the temperature dependence of the specific heat.

The results of investigations of the specific heat of rare-earth metals at temperatures above 0°C are cited in Table VIII. All the metals were investigated from 0°C up to their melting point. In the case of cerium, neodymium, samarium, praseodymium, and ytterbium the specific heat was investigated up to 1100°C. For these metals the temperature dependence of the specific heat of the high-temperature bodycentered cubic modification and in the liquid state is linear. For cerium, praseodymium, noedymium, samarium, scandium, and yttrium the specific heats for the liquid state have been calculated to be 9.35, 10.27, 11.60, 11.80, 9.00, and 10.50 cal/mole-deg respectively.

The thermal conductivity of the rare earths has not been sufficiently thoroughly studied. In all there is one paper<sup>[77]</sup> on the thermal conductivity, the data from which are presented in Table IX.

From the data of Table IX it can be seen that com-

	Specific heat, cal/mole-deg						
Element	$C_p = A + Bt + Ct^2  (t^{\circ}C)$						
	A	B · 10 <sup>3</sup>	C · 10 <sup>6</sup>	Temperatur interval, ° (			
a-Lanthanum	6,27	2,6	-	0-310			
B-L anthanum	6.45	3.0	_	310 - 864			
2-Lanthanum	10.30			864-920			
-Co-ium	6.37	2.95	1.19	0-730			
S-Corium	9.05			730-804			
a-Proceedymium	6.38	2.86	2.19	0-792			
B-Prae odymium	9.19		_	792-935			
g-Neodymium	6.52	2.49	3.26	0-862			
β-Neodymium	10.65			862-1024			
a-Semarium	11.80	0.955	*	0917			
8-Samarium	11.22			917-1072			
Furopium	6.20	4.0	_	0-826			
a-Gadolinium	6.63	2.3	—	30-1264			
B-Gadolinium	10.30			1264 - 1322			
a-Terbium	6.70	2.3		65-1317			
ß-Terbium	10.30			1317-1368			
Dysprosium	6.72	2.2		0-1380			
Holmium	6.45	2.2	-	0-1500			
Erbium	6.66	2.2	l	0-1525			
Thulium	6,50	2.1		0-1600			
a-Ytterbium	6.32	4.0		0-798			
$\beta$ -Ytterbium	10,30		- 1	798-824			
Lutetium	6.23	2.0		0-1675			
Scandium	6,00	1.1	-	0-1575			
Yttrium	6.13	1.5		0-1552			
*In the case of samarium $(-1.51 \times 10^3)/(t + 273.2)$ was sub-							

Table VIII.	Specific	heat of	rare-earth	metals	[13,17,48]	
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Table IX. The thermal conductivity of therare-earth metals

Metal	Thermal conduc- tivity at 26-30° C, cal-cm/sec-cm <sup>2</sup> ° C	Metal	Thermal conduc- tivity at 26-30° C, cal-cm/sec-cm <sup>1</sup> °C
Lanthanum Cerium Praseodymium Neodymium	$\begin{array}{c} 0.033 \pm 0.003 \\ 0.026 \pm 0.003 \\ 0.028 \pm 0.003 \\ 0.031 \pm 0.003 \end{array}$	Gadolinium Dysprosium Erbium Yttrium	$\begin{array}{c} 0.021 \pm 0.002 \\ 0.024 \pm 0.002 \\ 0.023 \pm 0.002 \\ 0.035 \pm 0.004 \end{array}$

pared with other metals the rare earths have a very low thermal conductivity. Such low thermal conductivity can cause local superheating of the sample surface in the determination of certain physical properties, in particular of the specific heat.

Magnetic properties. The rare-earth metals constitute a unique group of metals for the study of magnetic properties.

The rare-earth metals and their compounds include diamagnets, strong and weak paramagnets, ferromagnets, antiferromagnets, and ferrimagnets. Compared with the investigation of other physical properties, a large number of works has been devoted to the magnetic properties of the rare earths.

An interesting peculiarity of the rare earths is the fact that their effective magnetic moment corresponds almost exactly to the effective magnetic moment of trivalent ions (Fig. 7). This is explained by the fact that the 4f electrons which are the carriers of the magnetic moment are in a deep layer and are therefore unaffected by the valence electrons. The theoretical values of the magnetic moments of the rareearth metals were calculated by Van Vleck and Frank.<sup>[78]</sup> The theoretical and experimental values of the magnetic moments almost coincide except in the case of Sm<sup>+3</sup>, Sm<sup>+2</sup>, and Eu<sup>+3</sup> for which the theoretical values are somewhat low.

The rare-earth metals, with the exception of scandium, yttrium, lanthanum, ytterbium, and lutetium, have large paramagnetic susceptibilities compared with the common metals. In addition, it must be emphasized that the rare earths in the paramagnetic state follow the Curie-Weiss law only in a limited



FIG. 7. The dependence of the effective magnetic moment of the rare-earth metals on the atomic number.

temperature range. The paramagnetic susceptibilities of the metals belonging to the cerium subgroup are one to two orders of magnitude smaller than of those belonging to the yttrium subgroup. However, the laws for the change of the properties within the subgroups are identical; the susceptibility increases initially, and, having reached a maximum, decreases sharply.

The following rare earths have a ferromagnetic Curie point: europium, gadolinium, terbium, dysprosium, holmium, and erbium. All rare earths, with the exception of gadolinium, become ferromagnetic only at temperatures below 0°C. In the series of rare earths belonging to the yttrium subgroup the Curie point decreases from  $17 \pm 1^{\circ}C$  (for gadolinium) to  $-254 \pm 2^{\circ}C$  (for erbium).

Metallic gadolinium is of great interest with regard to its magnetic properties, since compared with the other rare earths it has the highest Curie point which is according to the latest data 17.1°C. In the paramagnetic region gadolinium obeys the Curie-Weiss law. The magnetic moment of the metal is close to the magnetic moment of its trivalent ion. The ferromagnetism of gadolinium was first observed by Urbain, Weiss, and Trombe.<sup>[79]</sup> According to their data the specific magnetization is 253.5 cgs emu which is considerably higher than the specific magnetization of iron under identical conditions (221 cgs emu).

In recent years the magnetic properties of gadolinium have been investigated using purer metal.<sup>[80,81]</sup> It has been established that in the temperature interval from 20 to 250°K the saturation moment of gadolium follows the  $T^{3/2}$  and not the  $T^2$  law, as had been previously determined by Trombe. It is interesting that gadolinium follows this law almost throughout the ferromagnetic interval, whereas other ferromagnets obey this law only in a narrow temperature range. Extrapolating these data to absolute zero, the effective moment is  $7.12\mu_{\rm B}$ , which is 2 percent higher than expected with account of the 4f electrons only. The effect of pressure on the Curie point has been studied by Patrick<sup>[82]</sup> who observed that at pressures from 0 to 8000 atmospheres every 1000 atmospheres lower the Curie point by  $1.2 \pm 0.05^{\circ}$ . We<sup>[83]</sup> measured the dependence of the magnetization  $4\pi I_S = f(H)$  of gad-

FIG. 8. The magnetization



olinium at room temperature and at the temperature of liquid nitrogen using a ballistic setup in a field of 10,000 Oe. The results obtained (Fig. 8) show that gadolinium is almost completely saturated in low fields and has a higher saturation than pure iron. Gadolinium exhibits the hysteresis characteristic of magnetically soft materials, the remanent induction amounting altogether to only a few percent of the saturation. A detailed investigation of the magnetic properties of gadolinium has been carried out at the Moscow State University by K. P. Belov on cast samples prepared by us.<sup>[84]</sup>

The temperature dependences of the magnetization, magnetostriction, Young's modulus, and the internal friction of dysprosium and gadolinium have been measured. Large anomalies have been observed in Young's modulus and in the internal friction at the ferromagnetic-antiferromagnetic transition point of dysprosium ( $\theta_1 = 85 - 88^{\circ}$ K); these anomalies are strongly influenced by a magnetic field. In this temperature range dysprosium has a large magnetostriction  $(\lambda_{\parallel} \approx 1000 \times 10^{-6})$  which is anisotropic  $(\lambda_{\parallel}$  and  $\lambda_{\perp}$  are of different sign). It has been established that in contrast to the antiferromagnetic-paramagnetic transition ( $\theta_2 = 178^{\circ}$ K), the transition at 88°K is connected with a change in the character of the magnetic interaction of the magnetic sublattices of dysprosium.

In the case of gadolinium a maximum of the magnetization in weak fields, a minimum of the coercive force and of the remanent magnetization have been observed at about 210°K. At this temperature the magnetostriction also vanishes. Near the Curie point there occurs also the anomalous magnetic behavior of gadolinium (compared with nickel and iron). The authors have stated the assumption that in this temperature range gadolinium is "partly" in the antiferromagnetic state.

The antiferromagnetic Néel point is observed in cerium, neodymium, samarium, terbium, dysprosium, holmium, erbium, and thulium.

The compiled data on the magnetic properties of the rare earths are presented in Table X. The magnetic properties are described in more detail in the original works: lanthanum, <sup>[18,25,85]</sup> cerium, <sup>[18,25,86,87,93]</sup> praseodymium, <sup>[25,87]</sup> neodymium, <sup>[87,88,91]</sup> samarium, <sup>[87,88]</sup> europium, <sup>[94]</sup> gadolinium, <sup>[70,81,86,95]</sup> terbium, <sup>[84,87,89]</sup> [87,89,96] dysprosium, [84,87,92] holmium, [87,90,98] erbium [95,99,100] thulium, [87,98,101] ytterbium, [25,87] lutetium, [30] scandium,<sup>[13,17]</sup> and vttrium,<sup>[85]</sup>

#### 4. MECHANICAL PROPERTIES

In connection with the search for new materials and wider utilization of metals and alloys with special physical properties, the rare-earth metals, yttrium and scandium assume an ever-growing interest, not only as alloving additions, but also as fundamental components of construction materials. At present the

	Magnetic suscep-	Constants of the Curie-Weiss equation $\kappa_g = C/(I-\theta)$			Effective magnetic moment		Characteristic points	
Element	tibility at 25° × A, 10 <sup>-6</sup> emu/mole	c, 10 <sup>-4</sup> emu °K/g	0, °K	Temperature interval, °C	theoretical (trivalent)	measured	Curie, • C (magnetic transition)	Néel, °C (antiferromag- netic transition)
a-Lanthanum γ-Cerium a-Praseodymium a-Neodymium a-Samarium Europium a-Gadolinium a-Terbium Dysprosium Holmium Erbium Thulium a-Ytterbium Lutetium a-Scandium Yttrium	$\begin{array}{c} 101\\ 2430 \\ 5320\\ 5650\\ 1275\pm25\\ 33100\\ 356\ 000\ ^{7}\\ 193\ 000\\ 99\ 800\\ 70\ 200\\ 44\ 100\\ 26\ 200\pm100\\ 71\\ 17\ .9\\ 8\ .08\\ 191 \end{array}$	$55.3^{2}$ $119.8^{4}$ $94.7^{5}$ $414$ $476$ $739$ $867$ $911$ $667$ $434$ $-$ $-$	$\begin{array}{c} -46^{3} \\ -21 \\ -4.3 \\ 866^{6} \\ +108 \\ +302 \\ +237 \\ +157 \\ +47 \\ +40 \\ +19 \\ +2 \\ -2 \\ -2 \\ -2 \\ -2 \\ -2 \\ -2 \\ -2$	$\begin{array}{c} -165+27\\ -195+230\\ -240+27\\ -150+20\\ +145+350\\ -36\\ +102\\ -36\\ +102\\ -36\\ +102\\ -36\\ +102\\ -36\\ +102\\ -36\\ -120+25\\ -36\\ +18\\ -220+1225\\ -78\\ +18\\ -220+1225\\ -78\\ -220\\ +1225\\ -78\\ -20\\ -20\\ +120\\ -20\\ +25\\ -78\\ -20\\ +120\\ -20\\ +25\\ -78\\ -20\\ +120\\ -20\\ +25\\ -78\\ -20\\ +20\\ +25\\ -78\\ -20\\ +20\\ +20\\ +20\\ +20\\ +20\\ +20\\ +20\\ +$	$\begin{array}{c} 0.00\\ 2.56\\ 3.62\\ 3.68\\ 1.60\pm0.05\\ 3.45\pm0.05\\ 7.94\\ 9.72\\ 10.6\\ 10.6\\ 9.6\\ 7.6\\ 4.5\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ \end{array}$	$\begin{array}{c} 0.49\\ 2.51\\ 3.56\\ 3.3\\ 1.74\pm0.02\\ 7.12\\ 7.95\\ 9.7\\ 10.64\\ 10.89\\ 9.5\\ 7.62\\ 0.41\\ 0.21\\ 0.14\\ 0.67\\ \end{array}$	None None 	None 

# Table X. The magnetic properties of rare-earth metals, yttrium and scandium <sup>[13,17]</sup>

<sup>1</sup>) This value was obtained at the first cooling to  $-270^{\circ}$  C; after the hundredth cooling it was  $2495 \times 10^{-6}$ .

<sup>2</sup>) The magnetic properties were measured up to 785°C; above 20°C cerium does not obey the Curie-Weiss law.

<sup>3</sup>) This value was obtained at the first cooling to -270°C; after the hundredth cooling it was -38.

4) Above 230° C praseodymium and neodymium do not obey the Curie-Weiss law.

<sup>5</sup>) Lock [<sup>25</sup>] found the constant (5.0 × 10<sup>-6</sup> emu/g) which must be added to the expression  $C/(T - \theta)$  in order to describe the magnetic behavior.

<sup>6</sup>) Samarium does not obey the Curie-Weiss law between -270 and 28° C.<sup>[25</sup>]

7) Extrapolated from 145 to 50° C

most promising in this respect is yttrium. In this connection the data on the mechanical properties of scandium and yttrium assume primary importance.<sup>[1]</sup>

In the literature the data on the mechanical properties of the rare-earth metals are incomplete. Their accuracy is affected by the purity of the metals, the experimental method, initial state (cast or thermally treated), and the orientation of the crystals. The main work on the mechanical properties of the rare earths, scandium, and yttrium was carried out by Savitskiĭ and Terekhova, <sup>[101,103,104]</sup> Spedding and Daane, <sup>[105]</sup> and Love. <sup>[106]</sup> The work on the mechanical properties of scandium and yttrium was surveyed by Simmons<sup>[107]</sup> at the symposium on the rare earths in November 1959 in Chicago.

For the majority of the rare earths, scandium, and yttrium the following mechanical properties have been determined: Young's modulus, the hardness, the strength, the plasticity in tension and compression at various temperatures, and also the capacity for plastic deformation by rolling and extrusion.

Elastic properties. The shear modulus, Young's modulus, Poisson's coefficient, and the compressibility were determined for the majority of the rareearth metals by Smith, Bridgman, and Love.<sup>[106]</sup> Smith <sup>[108]</sup> employed the method of measuring the

	Young's kg	modulus E, /mm²	Shear	Pois-	Compressibility $\beta$ , cm <sup>3</sup> /kg × 10 <sup>6</sup>	
Element	Data from [108]	Data from [106]	G, kg/mm²	coeffi- cient, ν		
Lanthanum Cerium Praseodymium Neodymium Samarium Gadolinium Terbium Dysprosium Erbium Thulium Ytterbium Ytterbium Yttrium	3915 3058 3592 3859 3480 5730 5864 6433 7474 	$7031 - 7734 \\ 4429 \\ 4922 - 9843 \\ -5625 \\ 5625 - 9843 \\ 7031 - 9843 \\ 11 660 \\ - \\ 6000 - 7000 *$	1518 1223 1378 1476 1286 2278 2327 2587 3016  717 2671	$\begin{array}{c} 0.228\\ 0.248\\ 0.305\\ 0.305\\ 0.259\\ 0.259\\ 0.261\\ 0.243\\ 0.238\\\\ 0.284\\ 0.265\\ \end{array}$	$\begin{array}{r} 3.24\\ 4.95\\ 3.28\\ 3.02\\ 2.56\\ 2.52\\ 2.45\\ 2.39\\ 2.11\\ \hline 7.12\\ 2.09\end{array}$	
*The avera	ge of value	s given by var	ious autho	rs.	I	

Table XI. Elastic properties of the rare-earth metals

propagation velocity of sound waves, Love determined Young's modulus from stress-strain curves. The data on the elastic properties are presented in Table XI. The values of Young's modulus according to Love are much higher than those of Smith.

It should be noted that in their elastic properties the light rare earths are most similar to magnesium and tin, whereas the heavy rare earths behave similarly to zirconium and titanium.

The elastic properties of lanthanum and cerium at various temperatures have been investigated in detail by Dashkovskiĭ and Savitskiĭ.<sup>[43]</sup> They studied the temperature dependence of the internal friction and the shear modulus for lanthanum and cerium up to  $600-670^{\circ}$ C. The curves showing the temperature dependence of the internal friction and the shear modulus for lanthanum are presented in Fig. 9. The observed maxima on heating (I) and cooling (II) are connected with the polymorphous  $\alpha \neq \beta$  transformation of lanthanum. The cooling curve reproduces the heating curve entirely but occurs at a lower temperature. A noticeable change of the shear modulus is observed in the temperature interval of the polymorphous transformation of lanthanum.

Figure 10 shows the curves of the internal friction and the shear modulus of cerium. Curve I corresponds to heating of a sample annealed for one hour at 600°C. Up to 250°C there occurs a linear increase of the internal friction, then a fast increase is observed, and in the region of 350-450°C a kink is observed in the curve. Above 500°C the internal friction increases very fast with increasing temperature. Curve III shows the temperature dependence of the internal friction of a cerium sample annealed for 20 minutes at 500°C. This curve has a clearly pronounced maximum at 380°C. On increasing the temperature or the duration of the anneal this maximum becomes smaller, broadens, and shifts towards higher temperatures. This shift occurs apparently on account of the increase of the grain size in annealing. The temperature dependence of the shear modulus of cerium is represented by curve IV. Up to 400°C there occurs a linear decrease, and further we observe a relaxation of the shear modulus which corresponds to viscous behavior of the grains.

The shear modulus for the same lanthanum and cerium samples was determined at room temperature. For lanthanum the shear modulus turned out to be  $1480 \pm 50 \text{ kg/mm}^2$ , and for cerium a value of  $1350 \pm 50 \text{ kg/mm}^2$  was obtained.

The method of investigating the mechanical properties. In view of the fact that the majority of metals belonging to the yttrium subgroup were obtained in quantities not exceeding tens of grams, our experiments were mainly conducted in the universal device for micromechanical experiments constructed by Savitskiĭ.<sup>[102,109]</sup>

In investigations of the effect of the temperature on the mechanical properties of the rare-earth metals use was made of logarithmic analysis of curves of the temperature dependence of mechanical properties. Since different polymorphous phases have different temperature coefficients of the properties, it becomes possible to determine the temperatures of the polymorphous transformations fairly accurately by plotting the properties on a semilogarithmic scale.<sup>[102]</sup> The data on the mechanical properties published at present in the literature refer mainly to rare earths with a purity of 98-99%.

Hardness. The experimental data obtained by various authors on the hardness of rare-earth metals at room temperature are given in Table XII. As can be seen no strict rule has been observed in the change of the hardness with the atomic number. A tendency is noted towards increasing hardness with increasing atomic number and melting point. The values of the hardness of individual rare-earth metals in the literature commonly differ strongly from each other because of impurity contamination, particularly by oxygen, because of differences in the method of deformation and in the grain size. For this reason it is so far impossible to establish the dependence of the hardness of the rare earths on their atomic number. Data on the hardness from single-crystal samples of the rare earths are so far unavailable. A decrease of the hardness (on the order of 10 units) has been ob-



FIG. 9. Temperature dependence of the shear modulus and the internal friction of lanthanum.

FIG. 10. Temperature dependence of the shear modulus and the internal friction of cerium.



Element	Hardness of casting H <sub>B</sub> , kg/mm <sup>2</sup>	Element	Hardness of casting H <sub>B</sub> , kg/mm <sup>2</sup>
Lanthanum Cerium Praseodymium Samarium Europium Gadolinium Terbium	$\begin{array}{r} 35-40\\ 25-30\\ 35-50\\ 35-45\\ 45-65\\ 15-20\\ 55-70\\ 90-120\\ \end{array}$	Dysprosium Holmium Erbium Thulium Ytterbrium Lutetium Scandium Yttrium	$\begin{array}{c} 55-105\\ 50-125\\ 60-95\\ 55-90\\ 20-30\\ 120-130\\ 95-120\\ 80-85\end{array}$

Table XII. Hardness of rare-earth metals.

served for the rare earths after annealing. Such a decrease in the hardness after annealing occurs as a rule in metals smelted in an arc furnace and having as a result of this a strongly strained structure. The hardness of rare earths deformed at room temperature increases by a factor of 1.5-2 on account of cold hardening.

The change in the hardness of lanthanum, cerium, and praseodymium (98% pure) with temperature has been investigated by Savitskii and Terekhova<sup>[102,103,104]</sup> in 1955, and that of gadolinium has been investigated at the Battelle Institute.<sup>[107]</sup> The hardness of lanthanum decreases with increasing temperature from 38 to 3.5 kg/mm<sup>2</sup> at 800°C (Fig. 11). A particularly strong softening of lanthanum has been observed at 550-600°C. In the case of cerium the hardness does not change appreciably up to 300°C; a sharp decrease of the hardness is observed at 350-400°C. The intensive decrease in the hardness of praseodymium on heating begins at 400°C. The change in the hardness of gadolinium pressed at 700°C from room temperature up to 925°C is shown in Fig. 12. Here too the sharp decrease in hardness is observed at 400-500°C. As can be seen from Figs. 11 and 12, in addition to polymorphism phenomena in the temperature variation of the hardness of lanthanum, cerium, praseodymium, and gadolinium in the interval from 100-300°C a deviation is also observed from the exponential dependence common for metals. In the case of the above metals there occurs at those temperatures a slowing down in the decrease of the hardness. This effect is, apparently, connected with the aging because of impurities due to the insufficient purity of the investigated metals. The effect of phase transformations, in particular polymorphous transformations, on the change of the hardness of metals and alloys as a function of the temperature is considered in detail in [102]. Most widely investigated is the hardness of yttrium. It has been established that the hardness of the purest yttrium varies within the limits from 30 to  $50 \text{ kg/mm}^2$ according to Brinell. Carlson investigated the effect of oxygen on the hardness of cast yttrium, [116] and established that the hardness of the latter increases with increasing oxygen content. According to the data of this investigation, the hardness of the yttrium after annealing depends also on a number of other factors: the size and orientation of the grains, the impurity content, the rate of cooling and the degree of stress in individual grains in the smelting in the arc furnace. Cast samples obtained by melting yttrium in tantalum crucibles and casting them in a vacuum induction furnace into copper molds are somewhat harder than yttrium smelted in an arc furnace.

Savitskiĭ and Terekhova investigated the change in the hardness of yttrium as a function of its purity, connected with the method of obtaining it.



FIG. 11. The temperature dependence of the hardness of a) lanthanum, b) cerium, and c) praseodymium plotted on linear and semilogarithmic scales.



The hardness of yttrium measured according to Brinell changes from 105 to 55 kg/mm<sup>2</sup> according to the method used in obtaining it. The least hard is yttrium obtained by vacuum distillation.<sup>[107]</sup>

An analogous investigation to determine the hardness as a function of the purity of the metal was carried out by us also for scandium. The hardness of industrial scandium  $(96-98\% \text{ pure})^{[103]}$  amounts to  $120 \text{ kg/mm}^2$ .

The mechanical properties of rare-earth metals under tension and compression. All known works on the strength and plasticity of scandium and yttrium are summarized in the article by Simmons.<sup>[107]</sup> The most extensive investigations of the strength and plasticity were carried out by the authors of <sup>[102,110,83,</sup> <sup>35,103,111,112]</sup>. Data on the strength and plasticity of the rare earths are given in Table XIII.

In analyzing the results obtained under tension and compression, a tendency is noted just as for the hardness towards increasing strength with increasing atomic number of the rare-earth metal. Metallic lutetium has the highest compressive strength. Rareearth specimens deformed 20—30 percent at room temperature have on the average a strength greater by a factor of 1.5 than the strength of cast specimens. The plasticity of the deformed samples decreases correspondingly. Recrystallization annealing of deformed samples decreases the strength to its initial value and increases the plasticity.

So far no data have been published on the dependence of the strength and plasticity of the rare-earth metals on the purity from individual impurities and on the addition of alloying addition. We have investigated the hardness and the deformability in cold rolling of technical yttrium with varying content of alloying addition (from 0.1 to 5 percent Cu, Mg, Ca, Zn, Al, Ti, Zr, Sn, V, Cr, Mo, and Fe). It has been established that yttrium is very sensitive to the introduction of alloying additions, even to comparatively small amounts of these. The largest effect is due to copper and magnesium with a content of 0.1 and 5

 
 Table XIII. Mechanical properties of rare-earth metals under tension and compression at room temperature.

		E	Data from [107]			Data of the authors			
Element State of metal		Yield point <sup>σ</sup> s, kg/mm²	Ultimate strength <sup>0</sup> B, kg/mm <sup>2</sup>	Relative elonga- tion δ, %	Stren (kg/m tensile <sup>0</sup> B	gth m <sup>2</sup> ) com- pres- sive <sup>o</sup> comp	Plastic ten- sile δ	city (%) com- pres- sive, E	
Lanthanum	cast forged	12.8 19.0	$\begin{array}{c} 13.3\\22.5\end{array}$	84	7.0	29.0	2—5	_	
Cerium	cast forged	9.3 11.2	10,5 15,4	24 17	12.0	30.0	5	33	
Praseodymium 	cast forged	$   \begin{array}{c}     10.3 \\     20.2   \end{array} $	11.2 21.9	10 7	9.5 —	29	20	31	
Neodymium	cast forged	16.8	$\begin{array}{c} 17.4\\21.2\end{array}$	11 2	13,0 —	25.0	1-2	36 	
Samarium	cast forged	11.4 18.5	$\begin{array}{r}12.7\\19.4\end{array}$	3 8	21.9	33.5	2	14.0	
Gadolinium	forged	27,4	39.7	7		-			
l'erbium	cast	-	~		-	71		16	
)ysprosium	cast forged	$\begin{array}{c} 22.9\\ 33.0 \end{array}$	$\begin{array}{c} 25.1\\ 43.6\end{array}$	$\frac{6}{3}$		52 —		20 —	
Io1mium	cast	22.6	26.4	5		51		20	
Erbium	cast forged	29.7 28.8	$\begin{array}{c} 29.8\\ 32.0 \end{array}$	4 7	29.0 	78.0	i 	22 —	
Thulium	cast				~~*	55		26	
	cast	6.7	7.3	6	6,6*		13 *	i I	
Lutetium	cast					102		12	
Scandium	cast					100		26	
					16	80		17	

	Cast						
	2	05° C	1	425° C			
Element	ultimate strength <sup>OB,</sup> kg/mm <sup>2</sup>	yield point σ <sub>S</sub> , kg/mm <sup>2</sup>	relative elonga- tion $\delta$ , %	ultimate strength <sup>O</sup> B, kg/mm <sup>2</sup>	yield point σ <sub>S</sub> , kg/mm²	relative elonga- tion δ, %	
Lanthanum Cerium Praseodymium Neodymium Samarium Gadolinium Dysprosium Holmium Erbium Ytterbium	$10.8 \\ 4.0 \\ 14.1 \\ \hline 14.8 \\ 12.6 \\ 21.6 \\ 24.4 \\ 7.2 \\ \hline$	$8.7 \\ 3.3 \\ 10.3 \\ - \\ 12.6 \\ 11.0 \\ 14.6 \\ 17.3 \\ 20.8 \\ 5.5 \\ 5.5 \\ \end{array}$	9.4 21.4 15.8 $-10,46.88.36.05.510.8$	$ \begin{array}{r} 4.7 \\ \\ 4.2 \\ 8.4 \\ 9.8 \\ \\ 17,6 \\ \\ \\ 17,6 \\ \\ 17,6 \\ \\ 17,6 \\ \\ 1000$	$2.6 \\ 4.1 \\ 4.0 \\ 7.7 \\ 8.5 \\ - \\ 20.2 \\ - $	$ \begin{array}{c} 21 \\ -29 \\ 13 \\ 5.6 \\ 11.3 \\ - \\ 6.8 \\ - \\ \end{array} $	
	Forged						
	,	205° C		425° C			
Element	ultimate strength <sup>0</sup> B, kg/mm <sup>2</sup>	yield point $\sigma_{\rm S}$ , kg/mm <sup>2</sup>	relative elonga- tion δ, %	ultimate strength °B, kg/mm <sup>2</sup>	yield point $\sigma_{\rm S}$ , kg/mm <sup>2</sup>	relative elonga- tion δ, %	
Lanthanum Cerium Praseodymium Semarium Gadolinium Dysprosium Holmium Erbium	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	

%

# Table XIV. Tensile properties of the rare earths at elevatedtemperatures [107]

percent. The mechanism of the action of alloying additions is connected in the first place with their ability to form with yttrium secondary phases, i.e., solid solutions, eutectic mixtures, and chemical compounds. In connection with the temperature dependence of the mechanical properties of the rare earths data are presented in the paper of Simmons <sup>[107]</sup> on the mechanical properties of the rare earths under tension at 205 and 425°C. These data are presented in Table XIV. Savitskiĭ and Terekhova investigated the plasticity in slow and shock compression, the tensile strength and plasticity of lanthanum in the temperature interval from 20 to 800°C, of cerium from 20 to 600°C, and of praseodymium from 20 to 800°C. The obtained data are shown in Fig. 13. The polymorphous transformations in the metals affect all the mechanical properties. This change in the properties is well exhibited in the graphs, especially when they are plotted in

FIG. 13. Temperature dependence of the strength and plasticity in experiments involving extension and compression for a) lanthanum, b) cerium, and c) praseodymium plotted on linear and semilogarithmic scales.



semilogarithmic coordinates. As is seen from the data presented, the plasticity of the rare earth increases sharply at the transformation to the cubic phase, confirming graphically the rule established by Savitskiĭ that the highest temperature modification of a polymorphous metal should be the most plastic one. [102]

As a result of the investigations which were carried out and the analysis of the obtained data, the following temperatures of maximum plasticity have been established: for lanthanum-600 to 700°C, for cerium -450°C, and for praseodymium-700 to 750°C. In the temperature variation of the properties of the tensile strength of lanthanum, cerium, and praseodymium a certain increase of the strength has been noted with increasing temperature up to 350-400°C, followed by a subsequent decrease. A similar phenomenon has been observed by Savitskii, Terekhova, and Baron in a number of brittle substances: germanium, cobalt, silicon, graphite, chromium, and chemical compounds (the disilicides of molybdenum, nickel, cobalt, and others). This phenomenon is most often observed in metals with a hexagonal or other more complicated crystalline structure, related to the effect of the temperature on the internal structure of the metals and alloys, and depends on the relation between the strength and plasticity of the metals. An important role is played here by the phenomenon of impurity aging. [102,103]

At the Battelle Institute experiments have been carried out on the mechanical properties of metallic gadolinium pressed at 540°C. The obtained values of the yield point, ultimate strength, the elongation, and Young's modulus as a function of temperature are shown in Fig. 14.<sup>[107]</sup> The study of the temperature variation of the tensile properties of gadolinium indi-



FIG. 14. Properties of gadolinium extruded through a die in tensile experiments as a function of the temperature.

cated the presence of a clearly pronounced aging effect at temperatures below  $350^{\circ}$ C, a fact which, as the authors note, is connected with the presence of impurities. The same kind of effect of impurities has been noted for praseodymium and samarium. These metals had a higher tensile strength on heating to  $200^{\circ}$ C than at room temperature.

The effect of impurities on the strength was investigated only in the case of yttrium.<sup>[107]</sup> It has been established that the strength of annealed yttrium changes relatively little with the contents of impurities or alloying elements. The largest strengthening effect was observed in the presence of hydrogen. Fluorine decreases somewhat the strength characteristics. Oxygen and nitrogen have almost no effect on yttrium, while a large carbon content increases the ultimate strength and decreases the elongation (Table 15). The data of <sup>[107]</sup> require checking.

From the aggregate of obtained data on the mechanical properties of the rare earths it follows that the heavy rare-earth metals of the yttrium subgroup have higher strength characteristics than the metals of the cerium subgroup, and that a general tendency towards increasing ultimate strengths with increasing atomic number of the rare-earth metal is observed.

Pressure treatment of rare-earth metals. It is nowadays possible by means of smelting with a consumable electrode, and casting into a copper, tantalum, or graphite mold in an inert atmosphere or vacuum to obtain rare-earth ingots weighing up to several tens of kilograms which can by various methods of pressure treatment be made into various semifinished products—sheets, rods, and cylinders.<sup>[106,107]</sup>

Table XV. Mechanical properties of metallic
yttrium with the addition of fluorine, oxygen,
carbon, nitrogen, and hydrogen <sup>[107]</sup>

Content of addition, wt %	Ultimate tensile strength <sup>TB,</sup> kg/mm <sup>2</sup>	Tensile yield point $\sigma_{s}$ , kg/mm <sup>2</sup>	Relative elonga- tion 8, %
Basic metal 0.10F 0.12F 0.13F 0.19F 0.20F 0.150 0.250 0.320 0.320 0.380 0.07C 0.12C 0.12C 0.12C 0.12C 0.12C 0.32C 0.34C 0.04N 0.05N 0.08N 0.10H 0.02H 0.06H	$\begin{array}{r} {\rm kg/mm^2} \\ 15.5 \\ 13.1 \\ 14.1 \\ 12.2 \\ 12.1 \\ 12.4 \\ 15.2 \\ 15.1 \\ 14.3 \\ 14.5 \\ 13.8 \\ 13.1 \\ 15.6 \\ 16.0 \\ 14.1 \\ 14.5 \\ 14.1 \\ 14.3 \\ 13.6 \\ 13.1 \\ 14.0 \\ 16.5 \\ \end{array}$	kg/mm <sup>2</sup> 6.8 5.95 5.25 5.4 6.9 7.1 7.7 7.7 6.4 5.8 6.9 7.8 7.4 9.1 6.1 6.4 6.15 6.5 5.7 6.4 7.4	25 27 28 27 25 27 25 27 25 27 23 28 28 28 28 29 20 11 12 30 17 28 28 29 20 11 12 30 29 26
0.10H 0.20H	17.1 —	8.9 8.9	26 —-

On account of the large number of slip planes in the cubic lattice of cerium, ytterbium, and europium, these metals can easily be worked by pressure compared with other rare-earth metals having a hexagonal lattice in which the strain occurs only by slipping in the direction of the basal plane. It should be remembered that metals with a hexagonal lattice which include most of the rare earths have a tendency to twinning. This is another important mechanism for the plastic deformation of these metals at ambient temperatures.<sup>[102]</sup> In the case of pure yttrium deformation twins appear in large numbers even in the preparation of metallographic sections. In analogy with other hexagonal metals the increased c/a ratio of the hexagonal lattice of some rare earths should have a strong effect on their plastic deformability. This problem has, however, not been altogether adequately investigated.

During the pressure treatment of rare earths at room temperature there occurs considerable cold hardening of the metals which prevents further deformation. This hardening is removed by intermediate annealing.

The fact that the rare earths react with the oxygen and nitrogen of the air renders their working difficult. For this reason the pressure working of rare-earth metals at elevated temperature must be carried out in cladding or in a protective atmosphere of inert gases. The behavior of rare-earth alloys in hot pressure treatment is in the first instance determined by their phase composition. Hard solutions based on rare earths will behave under strain like pure rare earths. One of us showed as early as in 1948 that metallic compounds of many metals that are brittle at ambient temperatures become very plastic and capable of changing their form and dimensions by means of hot pressure working <sup>[102]</sup> after being heated to 0.7-0.9 of their melting temperature. Undoubtedly this will also be true for metallic rare-earth compounds. Savitskiĭ, Terekhova, and Yampol'skiĭ<sup>[102,103]</sup> obtained by extrusion pressing rods of cerium and lanthanum of various diameters (1 to 5 mm). Klepfer and Snyder <sup>[114]</sup> worked out a method for obtaining foil of metallic thulium.

It has already been noted above that many rare earths are polymorphous. At the allotropic-transition temperatures the low-temperature hexagonal modifications, following Savitskii's rule, change to the more plastic high-temperature cubic modifications.<sup>[102]</sup> This phenomenon facilitates considerably the hot pressure treatment of lanthanum, cerium, praseodymium, neodymium, gadolinium, and terbium. As in other hexagonal metals, one should observe in the high-temperature pressure working of rare earths an increase in the deformability occuring as a result of the slipping of planes following the basal plane in their packing density, and in the first place of the pyramidal planes.<sup>[102]</sup> On the basis of experimental work of Soviet and foreign authors it has been established that the rare earths are distinguished by their good hot workability and in particular by hot pressing by extrusion. Compared with rolling, the pressing process is more economical for the production of items of a definite configuration; in addition, it requires less time for preparation and heating and it is connected with lesser oxidation of the metal.<sup>[106,107]</sup>

The forging process is connected with greater difficulties than pressing. Since the ingots obtained by arc smelting tend to crack, initial reduction must be carried out with great caution. It is best to use in forging pressed rods of the metal. To remove the hardening one must carry out intermediate annealing in an inert atmosphere.<sup>[106,107]</sup>

After the breakdown of the primary cast structure, the rare-earth billets can undergo hot rolling or stamping at temperatures above the corresponding temperatures of recrystallization. The optimum temperature for hot rolling and stamping of metallic yttrium is in the interval of 760-870°C. The capacity for cold working of the rare earths depends mainly on the quantity and the character of the distribution of impurities present in the metal. The most harmful impurities are oxygen and calcium. Metallic yttrium containing about 0.05% oxygen is relatively plastic and can be cold rolled with a reduction to 65-90% without edge cracking. Pressure working of yttrium containing 0.1-0.3% oxygen yields good results on heating to temperatures of the order of 900°C.<sup>[115]</sup> Of all rare earths ytterbium is most easily rolled into 0.1 mm thick sheets. Samarium can also be cold worked. The other rare earths, however, particularly those of the yttrium subgroup require preliminary hot working, and in cold working intermediate annealing is essential. In general it must be noted that the rare earths of the yttrium subgroup are technologically less workable than the elements of the cerium subgroup.

In cutting rare-earth metals the main difficulties appear in the mechanical treatment of the pyrophoric rare earths. In the mechanical treatment of the metal in which fine particles are produced there is danger of fire. It is recommended to carry out the working of items at low speeds, cooling the ingots with oil or dry kerosene.

The cold working of yttrium presents no difficulties. Yttrium is easily turned, bored, drilled, milled, and ground. In some cases, however, as a result of the liquation of impurities difficulties appear in individual operations of the mechanical treatment. Yttrium can easily be arc-welded with a tungsten electrode in an inert-gas atmosphere. The metal melted in the course of butt-welding does not have the tendency to crack. Much better results are obtained when welding yttrium with a filler wire. Metallic yttrium containing 0.1-0.3% oxygen tends to crack during welding.

# CONCLUSION

The rare-earth metals possess a unique set of physico-chemical properties which together with the raw-material resources of the rare earths assure them wide prospects in their use in instrument and machine building, in metallurgy, atomic technology, radio electronics, the chemical and glass industries, and also in agriculture and medicine. Hence the necessity for a considerable broadening and deepening of scientific research and experimental work in this direction.

The most important and timely problems of scientific investigation of the rare earths and their alloys should be the following: a final determination of their atomic and crystalline structure, of their physical constants obtained from single crystals of the purest rare earths, a detailed investigation of the physico-chemical properties of the rare earths (electrical, optical, magnetic, nuclear, mechanical and other properties) at high and low temperatures, at normal and high pressures, and also in various types of fields.

Very important is also the investigation of the crystal structure, the type of atomic bonding, the plotting of constitution and phase diagrams, the investigation of the properties of rare-earth alloys with each other and with other elements for the purpose of finding alloys and chemical compounds with special physico-chemical properties—superconductors, semiconductors, ferromagnets, cathode materials, neutron absorbers, accumulators for light energy, luminophors, catalysts, etc.

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