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The Crystal Structures and Lattice Parameters of High-Purity Scandium, Yttrium and the Rare Earth Metals*

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The crystal structures and accurate lattice constants of scandium, yttrium and the rare earth metals are given, and the values of their calculated mole-atomic volumes, densities, axial ratios and metallic radii are graphically compared. Expected variations due to the 'lanthanide contraction' and structure differences are noted, and additional irregularities in the axial ratio and metallic radii plots are indicated.

Introduction

The rare earth series represents a group of elements which are quite similar in their chemical and physical properties, the variations within the series being chiefly due to the so called 'lanthanide contraction'. As such, they are indeed desirable for investigations leading to an increased understanding of the behavior of the elements. High-purity metals have been prepared in this laboratory in relatively large quantities and many of their physical properties have been studied. Appreciable differences have been noted between the observed and previously reported values for their melting points, phase transformation temperatures and electrical resistivities.

Although several workers have investigated the crystal structures of scandium†, yttrium‡ and the rare earth elements§, the metals of increased purity now available, coupled with improved crystallographic methods and equipment, made the re-examination of these metals desirable. The mole-atomic volume, density, axial ratio and metallic radii of each element were calculated from the crystallographic data and were subsequently compared. To acquire this information, powder, single-crystal and precision back-reflection X-ray diffraction techniques were employed.

Experimental

Sample preparation and equipment

The metals studied were prepared in the Ames Laboratory by methods reported earlier (Spedding & Daane, 1954).

For the structure identification of scandium, yttrium and all the rare earths studied, except lanthanum, cerium, praseodymium and neodymium, metal filings annealed *in vacuo* at approximately 300° C. were examined with a 114·6 mm. diameter Debye–Scherrer camera. Bulk specimens of the four remaining elements were protected from the atmosphere by a thin coating of Krylon and were then examined with a Norelco diffractometer unit. In addition, single crystals of several elements were examined with a Weissenberg camera.

All of the back-reflection samples, except cerium, praseodymium, neodymium and gadolinium, were prepared by distilling the metals in a high-vacuum furnace ($\sim 2\times10^{-7}$ mm. Hg) in which the vapor was condensed on 0·0025 in. tantalum sheets which could be easily bent to fit the curvature of the precision back-reflection camera. The remaining metals were rolled to about $\frac{1}{16}$ in. thickness, formed to the radius of curvature of the camera by special dies, and then annealed *in vacuo* a few hours at approximately 300° C. An internal standard of KCl was added to praseodymium, neodymium, gadolinium and dysprosium by screening the salt (200 mesh) on to the diffracting metal surfaces freshly coated with a thin layer of collodion. There was insufficient europium metal available for a back-reflection examination; thus, its lattice constant was determined from its Debye–Scherrer powder pattern.

In all instances, filtered copper radiation was employed and the recommended film processing procedures were followed. The diffractometer and back-reflection camera were calibrated with silicon and KCl standards respectively.

Metal analysis

All of the metals studied were spectrographically analyzed for other rare earths and common impurities. In addition to the presence of neighboring rare earths,

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† Bommer, 1939*a*; Klemm, 1949; Meisel, 1939.

‡ Bommer, 1939*a*; Quill, 1932*a*, *b*.

§ Banister, Legvold & Spedding, 1954; Behrendt, 1954; Bommer, 1939*a*, *b*; Daane, Rundle, Smith & Spedding, 1954; Ellinger, 1955; Farr, Giorgi & Bowman, 1953; Hull, 1921; James, Legvold & Spedding, 1952; Klemm & Bommer, 1937, 1939; Lawson & Tang, 1949; McLennan & McKay, 1930; McLennan & Monkman, 1929; Quill, 1932*b*; Rossi, 1932, 1934; Schuch & Sturdivant, 1950; Schumacher & Lucas, 1924; Young & Ziegler, 1952; Ziegler, 1949; Ziegler, Young & Floyd, 1953; Zintl & Neumayr, 1933.

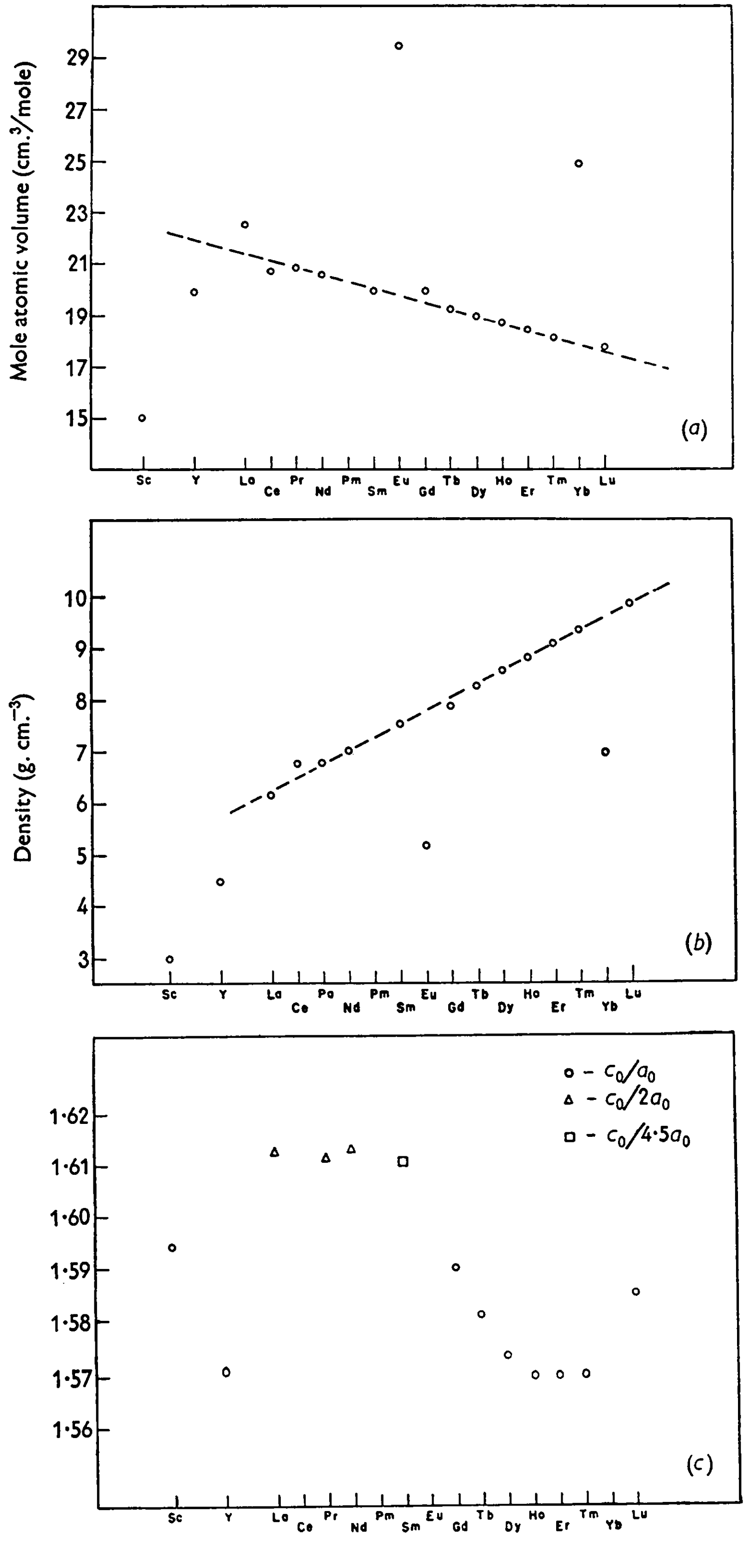

Fig. 1.

(*a*) Mole atomic volumes, and (*b*) densities of Sc, Y, and the rare earths.
(*c*) Axial ratios of Sc, Y, and the hexagonal rare earths.

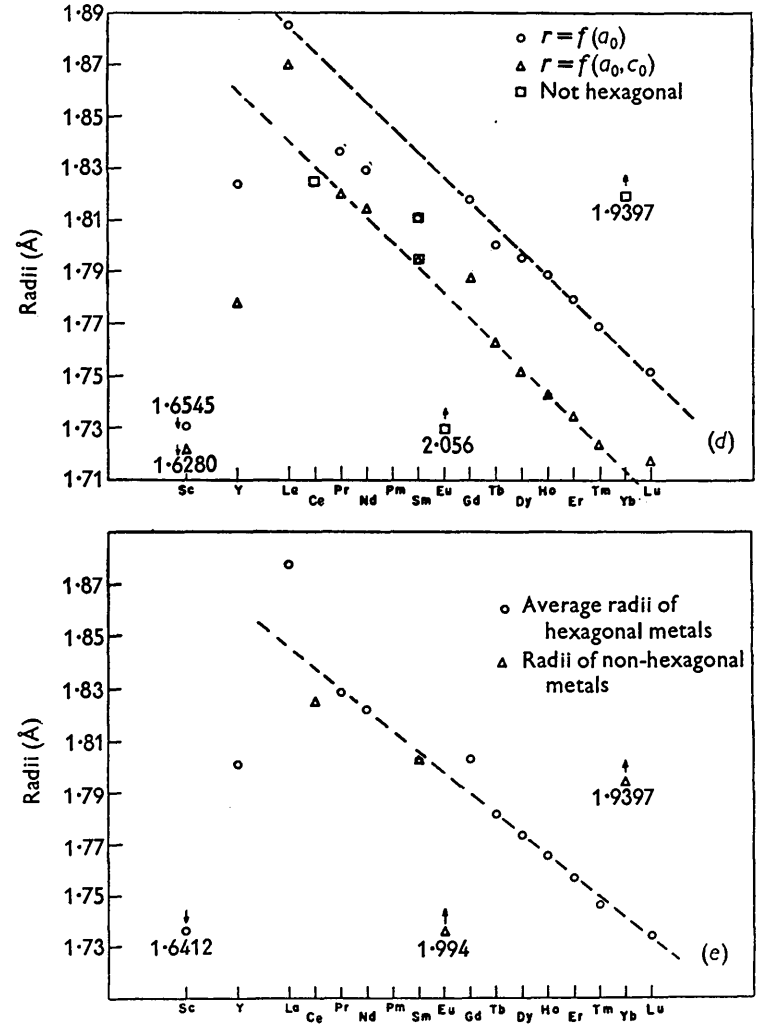

Fig. 1 (*cont.*)

(*d*) Individual metallic radii and (*e*) average metallic radii of Sc, Y, and the rare earths.

usually of the order of hundreths of percent, the chief impurities are calcium, tantalum, magnesium and silicon.

Lattice parameter calculation

Both Cohen's (1935) and Thewlis's (1952) methods were used to determine the lattice constants of the hexagonal metals, praseodymium, neodymium, gadolinium and dysprosium. After evaluating the results, Cohen's method was believed to be the more accurate and, therefore, only this technique was applied to the remaining hexagonal metals. The graphical extrapolation presented by Nelson & Riley (1945) was used to establish the lattice parameters of the cubic elements. The standard errors present in the values reported were calculated by the method devised by Jette & Foote (1935).

Results and discussion

Since all the structures observed, with the exception of lanthanum and praseodymium, were those previously reported, only the crystallographic data for these elements and neodymium are presented in Table 1. The data show the metals to have a h.c.p. structure but with c_0 values approximately double those cited previously. After re-investigating the structures of praseodymium and neodymium, Klemm & Bommer (1939) suggested their c_0 values be doubled to satisfy the intensity data and to account for some extra lines they observed, but they did not report the structure as such. Ellinger (1955) and Behrendt (1954) independently, in powder and single-crystal investigations, respectively, showed the necessity for doubling the c_0 value of neodymium. Comparison of the lanthanum and praseodymium data with those of neodymium readily indicates their similarities.

Table 1. *X-ray diffractometer data for* La, Pr *and* Nd

hkl	La *θ* (°)	Pr *θ* (°)	Nd *θ* (°)
100	13·61	13·95	14·08
101	14·11	14·48	14·54
004	14·63	15·07	15·12
102	15·48	15·92	15·99
103	17·54	18·07	18·17
104	20·22	20·78	20·90
105	23·25	23·92	23·97
110	24·07	24·79	24·86
106	26·50	27·34	27·43
114	28·70	29·55	29·69
202	29·20	—	30·19
008	30·40	31·32	—
206	—	38·40	38·58
109	—	39·25	39·45
211	—	—	40·25
212	39·45	—	40·95
118	40·50	41·89	42·09
1,0,10	42·41	43·95	44·13
216	—	48·50	48·80
304	48·60	—	50·67

The h.c.p. form of lanthanum was found to transform to the f.c.c. form on heating to about 260° C., the f.c.c. lattice constant being about 5·31 Å. Only after annealing 12–24 hr. below this temperature and then chemically etching the surface to a bright silvery luster which showed the large grains very plainly, could the distinct diffraction pattern of the pure h.c.p. form be observed. This transformation and the f.c.c. lattice constant will be reported in more detail in a future paper from this laboratory concerning the high-temperature forms of the rare earth metals.

The structures and lattice parameters of the metals studied are given in Table 2, from which their mole-atomic volumes, densities, axial ratios (where appropriate) and metallic radii can easily be calculated. These properties are graphically presented in Fig. 1(*a*)–(*e*). The effect of the 'lanthanide contraction' occurring in the rare earth series can be observed in the curves relating the mole-atomic volumes, densities and average metallic radii with atomic number. Representative of the differences among the rare earth elements which are becoming increasingly evident as data from precise, detailed investigations become available, are the irregularities observable in the plots of the individual metallic radii and axial ratios versus atomic number. Comparison of these values for the metals of similar structure reveals irregularities occurring at lanthanum, gadolinium, and lutecium. These three elements are related in that they have 4*f* shells which are unfilled, half filled, and filled respectively. The symmetry conditions resulting from these configurations may possibly be responsible for their different behavior but the data available do not afford a completely satisfactory explanation.

Assuming the atoms to be hard spheres, the axial ratio for a normal h.c.p. structure should be 1·633. Fig. 1(*c*) shows that scandium, yttrium and the hexagonal rare earths all have values below this, thus indicating asymmetric atoms. As can be observed in Fig. 1(*d*), the metallic radii of the hexagonal metals calculated for the atoms lying along the c_0 axis are considerably smaller than those calculated for the atoms lying in the basal plane of the unit cell. The directional bonding exhibited by these metals cannot be satisfactorily explained at this time.

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Table 2. *Lattice constants of* Sc, Y, *and the rare earth metals*

Element	Purity (%)	Crystal structure	Lattice constants a_0 (Å)	c_0 (Å)	Standard error a_0 (Å)	c_0 (Å)
Sc	99·6	h.c.p.	3·3090	5·2733	0·0001	0·0016
Y	99·4	h.c.p.	3·6474	5·7306	0·0007	0·0008
La	99·8	h.c.p.	3·770	12·159	0·002	0·008
Ce	99·9	f.c.c.	5·1612	—	0·0005	—
Pr	99·9	h.c.p.	3·6725	11·8354	0·0007	0·0012
Nd	99·8	h.c.p.	3·6579	11·7992	0·0003	0·0005
Sm*	99	rhom.-h.c.p.	3·621	26·25	—	—
Eu	98–99	b.c.c.	4·606	—	0·001	—
Gd	99·7	h.c.p.	3·6360	5·7826	0·0009	0·0006
Tb	99·9	h.c.p.	3·6010	5·6936	0·0003	0·0002
Dy	99·8	h.c.p.	3·5903	5·6475	0·0001	0·0002
Ho	99·4	h.c.p.	3·5773	5·6158	0·0001	0·0002
Er	99·8	h.c.p.	3·5588	5·5874	0·0003	0·0003
Tm	99·9	h.c.p.	3·5375	5·5546	0·0001	0·0004
Yb	99·9	f.c.c.	5·4862	—	0·0004	—
Lu	99·9	h.c.p.	3·5031	5·5509	0·0004	0·0004

* Values reported by Daane *et al.* (1954).

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Crystallographic Studies of Perovskite-Like Compounds. I. Rare Earth Orthoferrites and $YFeO_3$, $YCrO_3$, $YAlO_3$

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The orthoferrites of the trivalent ions Gd, Eu, Sm, Nd, Pr, La, and Y and the compounds $YCrO_3$ and $YAlO_3$ are isostructural. They belong to space group D_{2h}^{16}–*Pbnm* with four distorted perovskite units in the true crystallographic cell. X-ray and morphological data on these crystals are given and the relationships among them are discussed.

Introduction

Much X-ray work has been done on compounds with distorted perovskite structures, but, because it has for the most part been done on powders, it has not been definitive in all cases. Recently, J. P. Remeika (1956) of these Laboratories has succeeded in preparing single crystals (of size suitable for X-ray and optical examination) of a considerable number of compounds with general formula ABO_3 which are perovskite-like. One of these compounds is gadolinium orthoferrite, $GdFeO_3$, the crystal structure of which has been worked out in some detail (Geller, 1956) from single crystal X-ray data. It was found that the structure consists of four distorted perovskite pseudo-cells in an orthorhombic cell, the most probable space group being D_{2h}^{16}–*Pbnm*.*

The magnetic properties of the orthoferrite powders have been extensively investigated by Néel and his school (Néel, 1954; Pauthenet & Blum, 1954; Guiot-Guillain, 1953). Gilleo (1956*a*, *b*) has studied the magnetic properties of a crystal of $GdFeO_3$, and the magnetic structure of $LaFeO_3$ has been studied with neutrons by Roth (1954).

The work described herein deals with eight compounds isomorphous with $GdFeO_3$: the orthoferrites of Pr, Nd, Sm, Eu, La and Y; $YAlO_3$ and $YCrO_3$.

Crystallographic data on the perovskite-like compounds

The structure of $GdFeO_3$ was determined mainly from intensities obtained from Buerger precession camera photography of a ground plate crystal (see Geller, 1956). Single-crystal photographs (both Weissenberg and precession) were taken of $LaFeO_3$ and $YFeO_3$ crystals, using Mo *K* radiation. Powder photographs were taken of all the compounds with Cr *K* radiation.

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* See, however, the reservation in the Geller (1956) reference.