

Zur Kenntnis der Metalle der seltenen Erden

Wilhelm Klemm, Heinrich Bommer

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Picture the periodic table in nineteen thirty-seven. The lanthanides — that long row of elements tucked beneath the main body — existed almost entirely as oxides and salts. Chemists knew their chemistry but not their physics. Nobody had held gadolinium, or europium, or ytterbium as a pure metal and asked: what structure does it want to take? How does it behave in a magnetic field? Wilhelm Klemm and Heinrich Bommer, working in Danzig, decided to find out. They would reduce the chloride salts of every rare earth except holmium down to bare metal, one element at a time, and then measure what they had made.

The choice of method mattered. Klemm and Bommer followed what they called "das alte Wöhlersche Verfahren" — the old Wöhler procedure — reducing anhydrous rare-earth chlorides with molten alkali metals. The key word is anhydrous: bone-dry, oxide-free. Every starting chloride was dissolved in water and checked for turbidity; any haziness meant oxide contamination, and the batch was rejected. The reduction yielded not a compact ingot but a loose powder — a mixture of the rare-earth metal and the alkali chloride salt left over from the reaction. That powder turned out to be ideal. The alkali chloride served as an internal calibration standard in X-ray diffraction and as a diluent in magnetic measurements. And powder couldn't trap ferromagnetic impurities the way compact metals could, which had been a persistent problem in earlier studies. When the analyses came back, the numbers were tight: for lanthanum mixed with potassium chloride, the calculated lanthanum fraction is thirty-eight point thirty percent, and the found value ran between thirty-eight point one and thirty-eight point nine percent, totals clustering at ninety-nine point nine to one hundred point one percent. For neodymium, the calculated fraction is thirty-nine point twenty-one percent; they measured thirty-nine point three percent. The metals were real, and they were clean.

The apparatus itself was a sealed Supremax glass tube flushed with argon. The dry chloride sat at one end. A glass capillary loaded with freshly distilled alkali metal — sodium, potassium, rubidium, or cesium — was broken inside the device, and the metal melted and flowed into contact with the chloride. Reduction typically began below two hundred degrees Celsius. For most elements, heating to three hundred fifty or four hundred degrees Celsius completed the reaction and drove excess alkali to the far end of the tube. After cooling, the product was transferred under argon into sealed sample tubes for measurement.

Three elements refused to cooperate: samarium, europium, and ytterbium. All three showed a tendency to form dichlorides — stopping one step short of the fully reduced metal. Sodium was the worst reductant for samarium, giving a dark-red samarium dichloride instead of the metal. Heavier alkali metals, especially potassium, worked better. Temperature had to be kept below two hundred fifty degrees Celsius for these three, because even a modest temperature increase caused the reverse reaction — the metal re-oxidizing back into the chloride. At two hundred fifty degrees Celsius, distilling off the excess potassium took about twenty hours. Klemm and Bommer flagged this trio as exceptional. They would turn out to be the most theoretically interesting members of the series.

With pure metals in hand, Klemm and Bommer ran X-ray powder diffraction — the Debye-Scherrer method, using copper K-alpha radiation at one point five three nine angstroms and a camera diameter of fifty-seven point three millimeters. The alkali chlorides in each sample served as the internal standard, with the potassium chloride lattice parameter fixed at six point two seven seven angstroms. From the diffraction patterns, they read off lattice types and refined the lattice constants.

The central structural finding was clear. Most lanthanides crystallize in hexagonal close-packed form — atoms stacked in an ABAB layer sequence, each with twelve nearest neighbors. But two elements broke the pattern. Europium is cubic body-centered, with a lattice constant of four point five seven three angstroms and an atomic volume of twenty-nine point zero zero cubic centimeters. Ytterbium is cubic face-centered, with a lattice constant of five point four six eight angstroms, a twelve-fold atomic radius of one point nine three three angstroms, and an atomic volume of twenty-four point seven six cubic centimeters. For comparison, gadolinium — a typical member of the hexagonal majority — has an a equal to three point six two two angstroms and a c equal to five point seven four eight angstroms, with c over a equal to one point five eight seven, close to the ideal close-packed ratio. Europium and ytterbium were not just outliers structurally. They were dramatically larger than their neighbors.

That size difference is the key to the intellectual core of the paper. When Klemm and Bommer plotted atomic volume across the lanthanide series, they did not get a smooth decline. They got a curve with a general downward trend — the lanthanide contraction, driven by the gradual increase in nuclear charge across the series — punctuated by two sharp humps, at europium and ytterbium, and shallow dips at cerium, praseodymium, and terbium. Europium at twenty-nine point zero zero cubic centimeters sits far above its neighbors. Ytterbium at twenty-four point seven six cubic centimeters is also anomalously large for its position.

Klemm and Bommer read this curve as a valence map. They drew three reference curves through the data: one through the mainstream elements, representing trivalent behavior; one through barium, europium, and ytterbium, representing divalent behavior; and a third representing where a purely tetravalent metal would sit. The logic is direct — a divalent ion is larger than a trivalent one, so elements that are two plus in the metallic lattice will have inflated atomic volumes. Europium and ytterbium, sitting on the divalent curve, were acting like barium in their metals. Cerium, falling below the trivalent line, was hosting a fraction of four plus ions, which are smaller and pull the volume down. The atomic volume curve was not just a graph. It was a measurement of valence.

That interpretation needed independent confirmation. Klemm and Bommer turned to magnetic susceptibility — how strongly each metal responds to an applied magnetic field. The diagnostic power here is clean: quantum mechanics predicts a specific effective magnetic moment for each ionic charge state, so measuring the susceptibility and converting it to an effective moment tells you what oxidation states are present. For cerium, theory gives a nonmagnetic cerium four plus and a moment of two point five six Bohr magnetons for cerium three plus. Klemm and Bommer measured effective moments of one point eighty magnetons at ninety Kelvin, two point twenty-three at one hundred ninety-five Kelvin, and two point thirty-four at two hundred ninety-one Kelvin. The values climb toward the cerium three plus limit as temperature rises. Using a simple mixing rule, they estimated roughly equal amounts of cerium three plus and cerium four plus at ninety Kelvin, about seventy percent cerium three plus at one hundred ninety-five Kelvin, and about eighty-four percent cerium three plus at room temperature. The valence state of cerium in its own metal shifts with temperature. That is a striking result.

Then there is gadolinium. Klemm and Bommer confirmed that metallic gadolinium is the only rare-earth element in their series to display unmistakable ferromagnetism. The theoretical expectation for the gadolinium three plus ion gives a ferromagnetic moment of seven point zero Bohr magnetons and a paramagnetic moment of

seven point ninety-four magnetons. The experimental values cited in the paper are seven point fifteen and seven point ninety-five, respectively — agreement so close that it essentially proves the ion is entirely trivalent. Above the Curie temperature, gadolinium's susceptibility obeys the Curie-Weiss law: susceptibility equals a constant C divided by the quantity temperature minus a characteristic temperature θ . Below the Curie point, the response becomes field-strength dependent and the susceptibility climbs steeply. That is the ferromagnetic signature. No other rare earth in their study showed it cleanly.

Europium, despite containing divalent ions with the same four f electron count as gadolinium three plus, showed at most weak hints of ferromagnetism. Klemm and Bommer attributed this to geometry: europium in its body-centered cubic structure has only eight nearest neighbors rather than twelve, and the interatomic distances are larger, so the exchange interaction — the quantum-mechanical coupling that drives ferromagnetism — is much weaker.

What Klemm and Bommer achieved in Danzig was a methodological template as much as a set of measurements. By pairing X-ray diffraction with magnetic susceptibility on alkali-reduction products, they made the variable valence of the lanthanides experimentally tangible. The atomic-volume curve gave them a visual map of where valence departed from the trivalent norm. The magnetic moments gave them a quantitative check on that map, element by element. The two methods agreed. The rare earths were not a uniform block of trivalent metals with slowly shrinking radii. They were a series where europium and ytterbium preferred to donate only two electrons, where cerium flirted with giving up four, and where gadolinium alone among them ordered its magnetic moments collectively — the one ferromagnet hiding in a row of paramagnetic neighbors. The groundwork was laid one alkali-metal reduction at a time.

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