Boron-based atomic clusters mimic rare-earth metals

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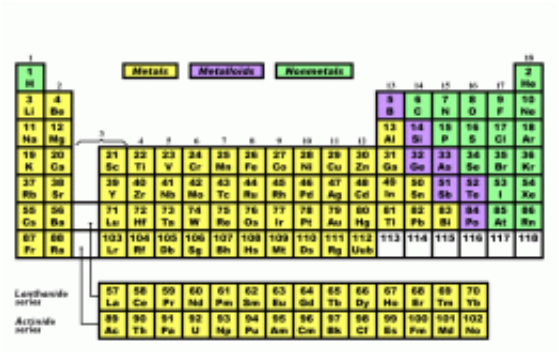

Rare Earth elements, found in the *f*-block of the periodic table, have particular magnetic and optical properties that make them valuable commodities. This has been particularly true over the last thirty years as more technologies use rare earth metals in their components, including audio speakers, computer hard drives, camera lenses, MRI imaging, television screens, and computer screens.

While these rare earth elements are found within the Earth's crust, the post-mining purification process can create hazardous waste, prompting some researchers to find cheaper and more environmentally friendly alternatives. Shi-Bo Cheng, Cuneyt Berkdemir, and A. W. Castleman, Jr. from the Department of Chemistry and Physics at Pennsylvania State University have shown that boron-doped lanthanide superatom clusters

mimic the valence electron configuration of certain rare earth elements, and may serve as rare earth analogs. Their work is published in the *Proceedings of the National Academy of Sciences*.

Cluster chemistry involves combining atoms or molecules in such a way that they are considered something in between an isolated atomic or molecular species and bulk material. This field gained prominence when nanomaterials and semiconductors became popular areas of research. Superatom clusters are a subcategory of cluster chemistry in which a cluster of atoms behaves as though it were single atomic species. The combined valence electrons in a superatom cluster are no longer identified with a particular nucleus, but behave as if they are the valence of a single atomic structure.

Early research into superatom clusters found that certain atoms or atomic combinations tended to cluster into particular numbers, known as magic numbers. Cheng et al.'s research looked at what they have dubbed a "magic boron" counting rule, in which boron combined with a lanthanide in a superatom cluster will contribute three unpaired electrons to the number of unpaired electrons in the lanthanide atom's valence.

Cheng et al. investigated whether the magnetic properties of the diatomic boron-doped lanthanum clusters and boron-doped neodymium clusters behaved like neodymium (Nd) and europium (Eu), respectively. They theorized that the spin characteristics of these particular superatom combinations should be similar to those of their isovalent rare earth counterparts, and would therefore display analogous magnetic properties. They first constructed the superatom cluster, then tested its valence properties using photoelectron spectroscopy and compared their experimental results to theoretical calculations.

Prior studies by this group demonstrated that TiO^-, ZrO^-, and WC^- were similar to Ni^-, Pd^-, and Pt^-, respectively. This work had established that

by simply counting the valence electrons of the atomic units comprising the cluster, certain clusters of atoms could behave as a superatom counterpart to isovalent, atomic anions. They wanted to apply this same technique to a boron-doped lanthanum, which should have six valence electrons in its neutral LaB cluster. Furthermore, if the LaB cluster does behave like Nd, then there should be four unpaired electrons in the cluster's valence, mimicking neodymium's magnetic properties.

Using photoelectron spectroscopy, Cheng et al. found that LaB adiabatic ionization energy (ADE, also the electron affinity) measurement was 0.909 +/- 0.025 eV. Vibrational frequencies were measured with four distinct peaks around the largest peak that represents neutralization of the LaB^- anion.

Experimental results were compared to theoretical calculations in which the lowest energy state was discerned from various spin multiplicities of both LaB^- and LaB. Theoretical calculations showed that the lowest energy conformation of LaB^- has three unpaired electrons (spin multiplicity of 4) and LaB has four unpaired electrons (spin multiplicity of 5). Theoretical vibrational energies correspond to the measured vibrational energies found using photoelectron spectroscopy. Additionally theoretical ADE and vertical detachment energy (VDE) of both LaB^- was very close to the experimental values with LaB^- ADE calculated to be 0.947 eV. This provides strong evidence that LaB likely has four unpaired electrons and six electrons, total, in its valence, which is analogous to Nd.

By combining the vibrationally-resolved photoelectron spectroscopy and high-level theoretical calculations, Cheng et al. have provided compelling evidence that LaB has four unpaired electrons and six electrons, total, in its valence, which is analogous to Nd. Similar experiments were further performed to examine whether such similarity is preserved between another boron-doped superatom cluster (NdB) and

its isovalent rare earth counterpart europium. Experimental and theoretical results confirmed that the lowest energy state of NdB has seven unpaired electrons, analogous to europium's valence.

More information: "Mimicking the magnetic properties of rare earth elements using superatoms" Shi-Bo Cheng, *PNAS* DOI: 10.1073/pnas.1504714112