Rare-earth dodecaborides: still cubic or not?

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The conductive, magnetic, optical, and mechanical properties of the rare-earth RB_{12} dodecaborides (R = Sc, Y, Tb, Dy, Ho, Er, Tm, Yb, Lu) are of significant interest both for basic research and for practical applications. The combination of metal conductivity with resistance to external influences makes them unique materials for use in extreme environmental conditions. In basic research, these compounds are conveniently used to study the properties caused by rare-earth metal ions.

The dodecaboride structure is formed by a strong framework of boron cuboctahedra (B_{12}). Metal atoms center the spacious B_{24} cavities between the cuboctahedra and are loosely coupled to each other. The structure of rare-earth dodecaborides is most often described as cubic, sp. gr. *Fm*-3*m*. The problem complicating the characterization of the structure and properties of dodecaborides is that the B_{12} cuboctahedra with the orbitally degenerate ground state are distorted by the cooperative Jahn-Teller effect, although to a very small extent.

The single-crystal structures of YbB_{12}, TmB_{12}, and LuB_{12} were studied in the temperature range 88–293 K, and HoB_{12} and ErB_{12} - in the range 88–500 K using high-resolution X-ray diffraction data to correlate structural changes with changes in the physical properties of the studied dodecaborides. Lattice deformations caused by the cooperative Jan-Teller effect were detected. A method is used for approximating the temperature dependences of atomic displacement parameters (ADP) using the extended Debye or Einstein models [1]. The breakpoints of the temperature dependences of ADP found for HoB_{12} ErB_{12} and YbB_{12}, in combination with nonmonotonic changes in the lattice parameters near critical temperatures T_c, indicate phase transformations revealed by diffraction data. Lattice instability and rearrangement of the phonon spectrum near T_c are accompanied by the observed changes in physical characteristics.

The proposed method for modelling of temperature depending on ADP is a sensitive structural diagnostics tool for detecting implicit phase transitions, quantum critical points, and quantum instabilities of various nature, leading to appearance of anomalies in the physical properties of crystals.

It was previously suggested that, under certain conditions, the formation of channels or stripes of conduction electrons in certain crystals could be associated with high-temperature superconductivity and colossal magnetoresistance. X-rays diffract from all types of electrons in the crystal, including conduction (delocalized) ones. The technical difficulty laying in the fact that conduction electrons have a low density and give a very weak diffraction signal was solved using special data collection and improved data processing techniques. The visualization of charge stripes in the studied dodecaborides using X-ray diffraction data was achieved by constructing difference Fourier syntheses of electron density without taking into account the crystal symmetry and by the complementary method of maximum entropy. Violations of the cubic symmetry of dodecaborides appeared in the orientation of the residual electron density in certain directions in the crystal. A correlation has been established between the anisotropic ED distribution and the anisotropy of conductivity [2].

The analysis of electron density distribution and the suggested visualization approach will provide the formation of systematic relationships between structure and physical properties and could be applicable to other crystals.

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