

atom positions based on the response ratio show that there are 1.1 % excited-state species in the crystal in which the I-I distance (3.82(2) Å) is contracted from the ground states (4.41(1)Å). While in the case of the discrete dimer complex $[\text{Cu}_2\text{I}_2(\text{PPh}_3)(\text{pyz})_2]$, two iodine atoms tend to move out of the $\{\text{Cu}_2\text{I}_2\}$ plane with opposite direction each other. This indicates that the $\{\text{Cu}_2\text{I}_2\}$ rotates around an axis containing two Cu atoms. This variety of the motions of $\{\text{Cu}_2\text{I}_2\}$ frameworks will be concerned with the geometry of the frame at the ground state and solid-state luminescent properties.

Keywords: synchrotron crystallography, photochemistry coordination compound, diffraction under non-ambient condition

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Structural changes in $\text{YBaCo}_4\text{O}_{7+\delta}$ monitored by variable temperature neutron powder diffraction

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In 2006 it was reported that YBaCo_4O_7 [1] (Y-114) is not oxygen-stoichiometric but absorbs oxygen up to $\delta = 1.5$ and then releases it upon heating (even in O_2 atmosphere) in a single, sharp step below 400 °C [2]. The oxygen storage capacity of Y-114 substantially exceeds those for the known oxides; $\text{CeO}_2\text{-ZrO}_2$: 1.50 mmol-O/ g_{catalyst} (500 °C) [3], Y-114: 1.88-2.82 mmol-O/ g_{catalyst} (340 °C). By means of in situ X-Ray Diffraction the unit cell of the oxygen-rich phase was identified [4]. This cell (o) is a super cell of the parent cell (h) where $a_o \approx \sqrt{3}a_h$, $b_o \approx c_h$, and $c_o \approx a_h$. This finding confirmed that oxygen absorption in Y-114 is, as expected, not based on a filling of crystallographic vacancies but rather an adaption of the structure to the increased temperature in presence of oxygen. These findings are confirmed in a very recent paper by Chmaissen et al. [5], where the determination and refinement of $\text{YBaCo}_4\text{O}_{8.1}$ structure is reported for the first time. Here, we will present our results on structural changes during oxygen intake and release in $\text{YBaCo}_4\text{O}_{7+\delta}$ as monitored by variable temperature neutron powder diffraction.

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Keywords: neutron powder diffraction, variable temperature, oxygen absorption

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Lattice parameter of microcrystalline gold in a broad temperature range

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The physicochemical properties of gold make that, despite its low abundance and high price, this precious metal has a number of important applications in technology. Moreover, It is one of standards used in X-ray diffraction for pressure and temperature calibration. The accuracy of temperature calibration depends on the knowledge of temperature variation of lattice parameter. Accurate knowledge of lattice-parameter temperature dependence leads to determination of thermal expansion behaviour. Up to now there was no detailed study of the gold lattice parameter covering the low and high temperature range. In the present study, the lattice parameter and the thermal expansion coefficient for the microcrystalline gold polycrystals were studied in detail in the broad temperature range, 10 - 1050 K, using a powder diffractometer at the B2 beamline (DORIS III Synchrotron Ring, Hasylab, DESY). The apparatus configuration allowed for collection of data with high resolution and low background. The wavelength was calibrated in situ, using a diamond standard. A commercial micrometer-size gold powder was mounted within thin-wall capillaries. The experimental value of the measured lattice parameter at 300 K is 4.07818 Å. The study provides reliable data on lattice-parameter temperature dependence, as supported by the close agreement of the derived thermal-expansion data, and of the resulting value of Debye temperature, with those reported in literature.

Keywords: lattice parameter, thermal expansion, gold

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Magnetic ordering in $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_2\text{O}_{5.5}$ for $x = 0.0$ and 0.1

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The crystal and magnetic structures of $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_2\text{O}_{5.5}$ for $x = 0.0$ and 0.1 have been studied by neutron powder diffraction in the temperature range from 20 to 365 K. The crystal structures of both compounds were found to be best described in space group *Pm3m* on a $2a_p \times 2a_p \times 2a_p$ unit cells where a_p refers to the lattice parameter of the cubic perovskite unit cell. The *a*- and *b*-axes were found to decrease and increase abruptly between 315 and 350 K as the temperature increases and the unit cell volumes exhibit signs of excess thermal expansion in the temperature range from 260 to 315 K. $\text{Dy}_{0.9}\text{Ca}_{0.1}\text{BaCo}_2\text{O}_{5.5}$ orders antiferromagnetically for $T \leq 305$ K into a G-type magnetic structure with a $2a_p \times 2a_p \times 2a_p$ magnetic unit cell. The magnetic behaviour of $\text{DyBaCo}_2\text{O}_{5.5}$ was found to be more complex as it exhibits two magnetically ordered phases. $\text{DyBaCo}_2\text{O}_{5.5}$ orders into a G-type magnetic structure at 260 and 290 K. A $2a_p \times 2a_p \times 4a_p$ magnetic unit cell was needed for indexing of the magnetic

reflections observed for $T \leq 230$ K. The low temperature magnetic structure was found to be antiferromagnetic with both pyramidally and octahedrally coordinated Co ions in the intermediate spin state. The high and low temperature magnetic phases were found to coexist at 230 K.

Keywords: magnetic perovskite materials, magnetic phase transitions, neutron powder diffractometry

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The 'gillespite-III' phase - the key for understanding a famous high-pressure phase transition?

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The phyllosilicate gillespite, BaFeSi₄O₁₀ (space group *P4/ncc*), has attracted attention in high-pressure research due to displaying striking features related to its ferroelastic phase transition at high pressures. In particular aspects related to symmetry and elastic softening associated with the observed transitions give reason to speculations on additional possible polymorphs at high pressure. The evaluation of lattice properties of gillespite-type analogue phases (with Cr²⁺ and Cu²⁺ substituting for Fe²⁺) by means of single-crystal XRD reveals first-order phase transitions in these analogue compounds, but the lattice symmetry of the high-pressure polymorphs clearly was found to be tetragonal. Both Raman and UV-VIS absorption spectroscopy investigations reveal features for the maintainance of local four-fold symmetries, in particular for the geometry of the planar MO₄-group, which is in contrast to the reported structural changes related to the orthorhombic high-pressure polymorph gillespite-II. Measurements of XRD intensities on the analogue-compounds in a diamond-anvil cell confirm the structure of a tetragonal high-pressure polymorph ('gillespite-III'), with a 3x3 superstructure showing a triplication of the tetragonal a-axis. Here we report on the single-crystal X-ray structural study based on a measurement in a low-background diamond-anvil cell, together with the results of measurements of in-situ high-pressure Raman spectroscopic investigations.

Keywords: high-pressure phase transition, gillespite structure, superstructure

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Crystallographic model of an atom and the dimension of real Euclidean space in Mendeleev's Table

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The dimension of real isotropic homogeneous Euclidean space is considered as the factor of self-organization of electrons of an atom into stable systems: into electron shells of an atom and periods of the Periodic Table of Chemical Elements. For revealing the role of the dimension of real space of it is considered the properties of the simplest polyhedron of n-dimensional space (a simplex of this space), the propositions of analytical geometry of three-dimension space. It

is constructed crystallographic models of arrangement of electron shells of an atom as regular systems of interacting Coulomb particles on a sphere of three dimensional space. The positions of electrons of shells are modeled by vertices of the antiprisms inscribed in a sphere. The change in the number of electrons in neighboring shells always only by four electrons is the result of the fact that (n + 1)th vertices of a simplex fix a sphere in n-dimensional space. It is considering the Pauli principle from point of view three-dimensionality of Euclidean space. The limited number of the electron shells of the ground-state of an atom (s-, p-, d-, f-shells) and the periods are the results of three-dimensionality of real space too. So three-dimensionality of real space along with its homogeneity and isotropy, centrosymmetric field of atomic nucleus, the properties of electrons as the Coulomb quantum indistinguishable particles are responsible for the number of chemical elements equals to 118 and the periodicity of their physicochemical properties. The finite number of stable systems of electrons and their complication with increasing the number of electrons led to simplicity and hierarchy in the structure of electron system of an atom.

Keywords: crystallographic model of an atom, three-dimensional real space, the Periodic Table of Chemical Elements

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Application of corepresentations to magnetic structures and displacive crystallographic transitions

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Corepresentation theory provides a physical basis for the description and understanding of many characteristics in the solid state. Most known from its application to magnetic ordering and phonon spectra, its language also describes electronic states and the symmetry changes associated with displacive phase transitions (commensurate and incommensurate). In this way they can be used to construct a generalised framework for symmetry changes in the crystalline solids. Use of such a common language makes clear couplings between order parameters that may otherwise appear unrelated, such as in multiferroic materials, and allows symmetry rules to be developed. The use of corepresentations has been limited due to difficulties in generating a reliable source of the representations that form the basis of their construction, and the mathematical subtleties related to their use in the projection of their associated basis functions and application of antiunitary symmetry. The number of possible symmetry types and the observation that basis vectors are phased according to the wavevector of the ordering, requires their in situ generation by computer codes and libraries. At present there is no standard for the characterisation of these symmetries and the characters of the irreducible representations and corepresentations must to be explicitly stated, or reference made to some work of reference. We have verified the automorphism of the tables of Kovalev and converted their settings to those now used by the IUCr, and released them as a library within the computer program SARAH. These relationships and the protocols for the generation of the correct basis vector spaces for the different situations are discussed.

Keywords: magnetic ordering, non-crystallographic symmetry, symmetry theory generalization and applications