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**X-ray Diffraction Study of Thermal Properties of Titanium Oxide**  
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Temperature dependence of microstructure of titanium oxide, TiO<sub>2</sub>, and the phase transition of anatase (A) to rutile (R) were studied by *in situ* X-ray powder diffraction and Raman spectroscopy, as well as by TEM and SAED techniques. The as-synthesized TiO<sub>2</sub> p.a. showed a gradual transition A → R during the temperature increase from ≈1200 K to ≈1570 K and during the temperature decrease to ≈600 K. High-energy ball-milling at room temperature induced a partial transition A→R. The transition continued during the temperature increase to ≈1370 K and during the temperature decrease, and is accompanied by sharpening of diffraction lines. Anisotropy of thermal expansion was noticed for both A and R. In the transition A→R, the nuclei of R are formed either throughout the A crystallites (in case of as-synthesized TiO<sub>2</sub> p.a.) or mainly in the interior of the A crystallites (in case of milled TiO<sub>2</sub> p.a.). These nuclei grow in number and size with a prolonged time of thermal agitation.

**Keywords:** titanium oxide, phase transition, thermal expansion

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**Influence of Grinding and Atmosphere on the Crystallization of ZrO<sub>2</sub> Gel**

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The influence of the grinding and the surrounding atmosphere on the thermal decomposition of zirconia gel has been studied. The XRPD analysis of the products obtained by thermal decomposition of zirconia gel at 500°C has shown that pure tetragonal phase is obtained if the gel decomposition is carried out under high vacuum or dry inert atmosphere. However, monoclinic zirconia results from the decomposition of the zirconia gel either under air or inert gas saturated with water vapor. A mechanism for the thermal decomposition of zirconia gel has been proposed from the study of the variation of the crystal size of the monoclinic and tetragonal zirconia phases formed as a function of the temperature and the surrounding atmosphere.

The thermal decomposition of the zirconia gel previously ground during two hours in a centrifugal mill leads to the formation of ZrO<sub>2</sub> with a percentage of tetragonal phase higher than 80% irrespective of the surrounding atmosphere. The stabilization of the tetragonal phase by grinding seems to be connected with the formation of tiny cubic or tetragonal zirconia crystals that cannot be observed by XRPD. The results obtained by DSC supports this conclusion. Thus, the crystallization enthalpy determined for the as prepared gel was equal to -128 ± 7 J/g, in good agreement with literature, while the crystallization enthalpy for the ground gel amounted only -12 ± 2 J/g.

**Keywords:** zirconia gel, crystallization mechanism, crystal size

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**Magnetic Study of Intermetallic Ce<sub>1-x</sub>Tb<sub>x</sub>Mn<sub>2</sub>Ge<sub>2</sub> (0 ≤ x ≤ 1) Compounds**

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In this study, the crystal structure and magnetic properties of Ce<sub>1-x</sub>Tb<sub>x</sub>Mn<sub>2</sub>Ge<sub>2</sub> (0 ≤ x ≤ 1) compounds have been investigated by means of x-ray powder diffractions and magnetization measurements. X-ray diffraction patterns at room temperature indicated that all compounds

are single phase and crystallize in the ThCr<sub>2</sub>Si<sub>2</sub> type structure with space group I4/mmm. With increasing x, lattice parameters and unit cell volume have decreased linearly, obeying the Vegard's law. The magnetic properties of Ce<sub>1-x</sub>Tb<sub>x</sub>Mn<sub>2</sub>Ge<sub>2</sub> were investigated by means of field-cooled and zero-field-cooled magnetization measurements in the temperature range 5 K ≤ T ≤ 600 K. In CeMn<sub>2</sub>Ge<sub>2</sub>[1] and TbMn<sub>2</sub>Ge<sub>2</sub>[2], the interlayer magnetic coupling in the Mn sublattice is, respectively, ferromagnetic and antiferromagnetic below about 350 K. At low temperatures, Tb sublattice orders and reconfigures the ordering in the Mn sublattice while Ce does not order at any temperature. In this study, we investigated the variations in the magnetic properties of Ce<sub>1-x</sub>Tb<sub>x</sub>Mn<sub>2</sub>Ge<sub>2</sub> as a function of rare earth concentration by examining the evolution of the features in the temperature dependence of the magnetization. The results are summarized in the magnetic phase diagram.

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**Keywords:** magnetic transitions, layered magnetic structures, rare earth compounds

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**Phase Transitions and Crystal Dynamics at Low Temperature of Alpha-U and <sup>4</sup>He**

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Uranium metal includes temperature dependent elastic constants with the occurrence of a charge-density wave (CDW). At T<sub>0</sub> < 43 K (lower limit of stability of the structure) a transition involving modes for which **q**<sub>CDW</sub> = <q<sub>x</sub>, q<sub>y</sub>, q<sub>z</sub>> occurs. Domains are formed in different parts of the crystal in relation with the lowering of symmetry. The electronic instability which causes Kohn anomaly also triggers the displacive (Peierls) transition. The band gap created at the Fermi surface geometry determines the wave vector of the Kohn anomaly and of the incommensurate distortion. Inelastic neutron scattering<sup>1)</sup> has confirmed the existence of a transition to the incommensurate low-temperature condensing soft mode with a modulation wave vector **q**<sub>min</sub> = [0.497 (1), 0.13 (1), 0.21 (1)]. The helicoidally motion of **q**<sub>CDW</sub> (43 → 20 K) to the clock-side around **a**<sup>\*</sup> (measured by Laue elastic diffraction) has been observed in continuity of the variation of **q**<sub>min</sub> (65 → 44 K) (recently measured inelastic scattering with three-axis spectroscopy) and **q**<sub>min</sub> ≅ **q**<sub>CDW</sub> at T<sub>0</sub> = 43 K.

In situ phase transition from solid α (hcp) to solid γ (bcc) occurring in pure <sup>4</sup>He has been investigated in (P, T) plane at 27.5 bar, 1.65 K, by neutron three-axis spectrometer and Laue diffraction. Dynamic solid – solid transformation<sup>2)</sup> of mosaic crystal grains were clearly observed with the two techniques continuously followed in time and observed as motion of macroscopic small angle grain boundaries of quantum crystal.

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**Phase Transition of C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub>Zr[(CH<sub>3</sub>COO)<sub>3</sub>]<sub>2</sub>·4 H<sub>2</sub>O**

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In the course of our investigations on zirconium-nitrioltriacetates of alkyldiamines we found in the title compound, 2-ethylammonium-ethylammonium-zirconium bis(nitrioltriacetato)-tetrahydrate, anomalous thermal and elastic properties between 288 und 293 K. Above 293 K, this species exhibits space group P2<sub>1</sub>/n with lattice