

discussed with respect to complexity and phase formation.

[1] T. Weber, J. Dshemuchadse, M. Kobas, M. Conrad, B. Harbrecht, W. Steurer **2009**. *Acta Cryst. B*, *65*(3), 308–317. [2] M. Conrad, B. Harbrecht, T. Weber, D. Y. Jung, W. Steurer **2009**. *Acta Cryst. B*, *65*(3), 318–325.

**Keywords:** intermetallic, cluster, superstructure

## MS98.P03

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### Unusual orbital and atomic ordering in tetragonal phase of MgTi<sub>2</sub>O<sub>4</sub>

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It is theoretically shown that the structure of the tetragonal phase MgTi<sub>2</sub>O<sub>4</sub> contains metal pico- and nanoclusters: two types of dimers Ti<sub>2</sub>, two types of helices along the axis of the second and fourth-order of tetragonal cell and two types of one-dimensional infinite strands of titanium ions. Such unusual structural features of magnesium titanite arise due to atomic and d-orbital ordering.

A theory of structural phase transition in MgTi<sub>2</sub>O<sub>4</sub> is presented: the symmetry of the order parameter, thermodynamics and mechanisms of formation of atomic and orbital structure of the low-symmetry phase MgTi<sub>2</sub>O<sub>4</sub> are studied. The critical order parameter, which induces a phase transition, has been stated; it is shown that the calculated structure of the tetragonal phase MgTi<sub>2</sub>O<sub>4</sub> is formed as a result of the displacements of magnesium, titanium and oxygen, the ordering of oxygen atoms, ordering d<sub>xy</sub>, d<sub>xz</sub>, d<sub>yz</sub> – orbitals. It is proved that the contribution of non-critical representation in the ions displacements is insignificant.

In the framework of the sixth degree of the components of the order parameter of the Landau theory the possible phase diagram is constructed and it is shown that the changes of phase states can be carried out as a result of phase transitions of second and first order: high-symmetry phase borders with two low-symmetry phases along the lines of transitions of second order, and the border between low-symmetry phases is the line of the phase transitions of first order.

The proposed theory is in accordance with experimental results [1].

[1] M. Schmidt, W. Ratcliff, P.G. Radaelli, K. Refson, N.M. Harrison, S.W. Cheong. *Phys. Rev. Lett.* **2004**, *92*, 056402-1–056402-4.

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### Self-assembly of nanoparticles into planar modulated superstructures

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The advance in the synthesis of nanoparticles and colloids opens up the possibility to use them as building blocks for self-assembling novel materials. Ordered structures are especially interesting because they have unique photonic and electronic properties. Among the most complex ordered phases are commensurately and incommensurately modulated crystals. Although frequently found on the atomic scale in

the bulk and as ordered structures of noble gases in adsorbed layers, modulated phases have so far not been known to self-assemble with nanoparticles.

Here, we use computer simulations to study a two-dimensional system characterized by a simple isotropic interaction that could be realized in future with building blocks on the nanoscale. We find that the particles arrange themselves into planar hexagonal superstructures whose superlattice vector can be tuned reversibly by changing the temperature. Thermodynamic stability is confirmed by calculating the free energy with a combination of thermodynamic integration and the Frenkel-Ladd method. Different contributions to the free energy difference are discussed.

[1] M. Engel, *Phys. Rev. Lett.* **2011**, *106*, 095504.

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## MS98.P05

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### Crystal structures of new superconducting compounds, LnT<sub>2</sub>Zn<sub>20</sub> (Ln = La, Pr, T = Ru, Ir)

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In recent years, the cluster compounds and/or the compounds having cage-like substructure have attracted much attention not only in chemistry field but also in field of solid-state physics, to show rich interesting properties, since the discovery of fullerenes and fullerides. For example, in solid-state field, these compounds (especially, having rattled atoms in the cluster/cage structure) show various kinds of physical properties such as strong electron-phonon coupling superconductivity [1], heavy fermion behaviour [2], and thermoelectricity with glass-like thermal conductivity [3].

Last year, we found new superconducting compounds; LnT<sub>2</sub>Zn<sub>20</sub> (Ln = La, Pr, T = Ru, Ir), showing superconducting transitions at T<sub>c</sub> around 0.2 K (LaRu<sub>2</sub>Zn<sub>20</sub>), 0.6 K (LaIr<sub>2</sub>Zn<sub>20</sub>), and 0.05 K (PrIr<sub>2</sub>Zn<sub>20</sub>). Especially, PrIr<sub>2</sub>Zn<sub>20</sub> is the second example of superconductor in the intermetallic compounds containing Pr atom. [4] Before taking superconducting state, these compounds take structural transitions, but do not have any magnetic transitions. At room temperature, the crystal structure of these compounds basically takes cubic CeCr<sub>2</sub>Al<sub>20</sub>-type structure (Fd-3m). [5] Details of the crystal structure are not so clear.

To understand the detail of this crystal structure, we carried out single-crystal diffraction technique at 293 K. Our used single crystals are grown by Zn self-flux method. [6] In the structure, Ln atom locates in the cage structure formed by 16 Zn atoms. On the other hand, T atom is surrounded by 12 Zn atoms forming another cage structure. Both Ln and T atoms locate at crystallographically independent sites. However, some of Zn sites show the site disordering behaviour. More details will be presented.

[1] E.D. Bauer, N.A. Frederick, P.-C. Ho, V.S. Zapf, M.B. Maple: *Phys. Rev.* **2002**, *B 65*, 100506. [2] See, for example, *J. Phys. Soc. Jpn.* **2008**, *77 A*, and references therein. [3] (Ed.) M.G. Kanatzidis, S.D. Mahanti, T.P. Hogan, *Chemistry, Physics and Materials Science of Thermoelectric Materials: Beyond Bismuth Telluride*, Kluwer Academics, Plenum Publishers, New York, **2003**. [4]