

discussed with respect to complexity and phase formation.

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**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].

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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.

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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.

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**MS98.P06**

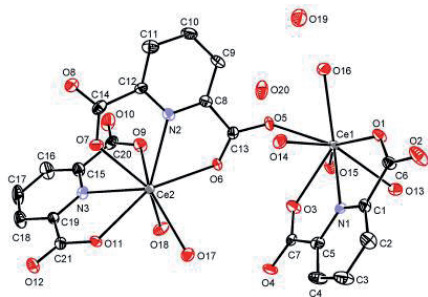
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**Structure of a polymeric Ce(III) complex containing pyridine-2,6-dicarboxylic acid**

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Coordination polymers of rare earth elements have received significant attention in recent years because of their potential optical, magnetic, and porous properties, especially for the carboxylates [1–4]. The large ionic radii of rare earth elements together with the coordination flexibility of lanthanide ions can lead to unusual structural topologies and new framework families [5].

Here we report the synthesis, characterization and crystal structure of the polymeric  $\{[Ce(pydc)_3(H_2O)_8] \cdot 2H_2O\}_n$  complex (**I**), obtained from the reaction of Cerium(III) nitrate with the pyridine-2,6-dicarboxylic acid, dipicolinic acid (pydcH<sub>4</sub>) and 2-aminopyrimidine (ampy) in 1:1:1 molar ratio in basic media. Polymeric complex was characterized by FT-IR spectroscopy and X-ray diffraction. X-ray crystal structural analysis reveals that the compound belongs to the triclinic space group  $P\bar{1}$  with cell parameters  $a = 10.407(4)$  Å,  $b = 11.795(5)$  Å,  $c = 13.770(6)$  Å,  $\alpha = 93.852(2)^\circ$ ,  $\beta = 111.142(2)^\circ$  and  $\gamma = 111.105(2)^\circ$ . The molecular structure consists of two crystallographic independent pairs of Ce<sup>III</sup> ions in the unit cell (Fig. 1). The coordination polyhedron of the ten-coordinated Ce1 ion is a distorted bicapped square antiprism comprised of O1 and O2 bridged atoms from pydc ligand coordinated to the Ce1 ion of the neighboring unit, N1,O3,O4 atoms of the one dipicolinate ligand, bridged O5 atom of pydc ligand coordinated to the Ce2 ion of another neighboring unit, O13, O14, O15 and O16 atoms of the water molecules. The Ce2 ion is in slightly distorted tricapped trigonal prism being coordinated by N2, O6, O7 and O8, O11 and N3 atoms from two dipicolinate ligands, bridged O11 atom from pydc linked to the Ce2 ion of the neighboring unit, O17 and O18 atoms of the water molecules. In the crystal structure, a wide range of noncovalent interactions consisting of hydrogen bonding (of the types of O–H...O and C–H...O) and ion pairing interactions connect the various components into a supramolecular structure.



**Fig. 1.** ORTEP plot showing the coordination environments of cerium ions in **I**.

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**Reciprocal space statistical thermodynamics of inhomogeneous disordered systems**

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Within the last decades a lot of efforts were made in order to understand the nature of dynamical heterogeneities in disordered systems, e.g. supercooled liquids, amorphous alloys. Nevertheless the nature of the amorphous state formation, a fundamental problem of condensed matter physics, is not completely understood.

It has been recently shown [1] that the dynamic origin of heterogeneous dynamics might be a result of critical-like fluctuations of static structural order. This is a concept that counters the currently accepted trend.

Here we present a reciprocal-space approach for inhomogeneous systems, based on the ring approximation [2], [3]. This concept deals with cooperative reciprocal-state modes and takes into account their statistical coupling, both in atomic interaction and in mutual arrangement of particles, much unlike traditional real-space statistical thermodynamic approaches.

Using the ring approximation in the framework of kinetic atomic density functional approach [4], we describe configurational self-organization in the amorphous state. The Fourier transform of the relaxation time is given by the following expression:

$$\tau(\mathbf{q}, T) \sim -kT/[D_0(T)q^2 V_{eff}(\mathbf{q}, T)], \quad (1)$$

where  $\mathbf{q}$  is a reciprocal lattice vector, temperature-dependent coefficient  $D_0(T)$  accounts diffusive properties of the system,  $V_{eff}(\mathbf{q}, T)$  is the “renormalized” effective pairwise interaction potential [1], and it is taken into account that interference of atomic interaction modes with different wave vectors takes place. In the mathematical expression above it is also assumed that the temperature range is significantly lower than the structural instability point, also called spinodal point.

Equation (1) leads to the conclusion that the dominant mode, corresponding to the minimal negative value of  $V_{eff}(\mathbf{q}, T)$ , develops the most intensively. For the Dzugutov-like potential, widely used in simulations of the amorphous state, the function  $V_{eff}(\mathbf{q})$ , exhibits a flat region of the dominant modes for a certain range of potential parameters. Consequently, a set of these modes possesses the same value of relaxation time. This corresponds to formation of a highly inhomogeneous structural state. Interference of the dominant modes leads to the long-living ordered structural states, e.g., clusters, recently revealed by X-ray cross-correlation analysis [5] of coherent scattering data.

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