

**COMBINED COHESIVE ENERGY AND DIFFRACTION DATA
REFINEMENT OF D-AINiCo QUASICRYSTAL STRUCTURE**

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We describe a systematic approach to quasicrystal structure refinement on the basis of structural energy, combined with the diffraction data input. We choose as an example the decagonal quasicrystal AlNiCo, for which both high-quality diffraction data, and effective ternary pair potentials needed for evaluation of energies, are available. The ensemble of structures we admit is restricted to periodic stacking of 2D rhombus tilings. The rhombi are decorated by candidate sites that are available for atoms to occupy like a lattice gas. In a finite-temperature Monte Carlo simulation, atoms may hop from one site to another, or pairs of atoms occupying different sites may swap. Simultaneously, the rhombus tilings are independently reshuffled via the standard local 'tile-flip' rearrangements. Each site is additionally assigned continuous positional degrees of freedom; these are constrained by point symmetries of the local tiling pattern, with which a site was associated. The Metropolis Monte Carlo scheme is combined with nonlinear least square fitting procedure to minimize an objective function combining structural energy with the weighted R-factor computed from the diffraction data.

Keywords: QUASICRYSTAL ALNiCo REFINEMENT

**MOLECULAR DYNAMICS STUDY OF AN INCOMMENSURATELY
MODULATED STRUCTURE**

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We have used molecular dynamics (md) to simulate the incommensurate structure of hexamethylenetetramine, which has been previously solved from single crystal x-ray diffraction in the superspace approach. In md, the time evolution of a set of interacting atoms is obtained by integrating their Newton equations of motion. Interactions between atoms include non-bonded potentials (the Lennard-Jones 9-6 potential and the Coulomb potential) and bonded potentials (bond stretching potential, bond angles potential, torsion potential and out-of-plane potential). All potential parameters were derived from the consistent force field (cff91), a second-generation force field. Intermolecular or non-bonded parameters are obtained by fitting to experimental crystal lattice constants and sublimation energies. The applied parameters are especially adapted for a large number of organic molecules and were successfully used to predict lattice parameters and sublimation energies for crystals. The Coulombic potential for which a simple truncation is not justified due to the slow convergence of the sum of terms decaying as $1/r$ was obtained by the Ewald method. The simulation of the incommensurate structure was carried out in the temperature range from 15 K to 580 K with a time step of one femto-second. The starting structure at 298 K was a commensurate approximation closest to the incommensurate structure. In order to get lattice parameters close to the experimental ones, a unique compensating pressure tensor was applied during the simulations. Different simulated phases appear at various temperature ranges, one of which is incommensurate. The current md simulation reproduces well the experimental diffraction results.

Keywords: MOLECULAR DYNAMICS INCOMMENSURATE
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**COMPARATIVE STRUCTURAL REFINEMENT OF DECAGONAL
AL-CO-NI - EDAGAWA SUPERSTRUCTURE**

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The relationship between the basic decagonal Al₇₁Co₇Ni₂₂ phase and the related decagonal Edagawa superstructure [1,2] (Al₇₁Co₁₃Ni₁₆) has been intensively studied. A thorough superspace-based structure refinement of both phases [3,4] based on high-resolution synchrotron X-ray data clarifies their structural relationship. The basic phase, with only 6-10% Co, stable over 950°C, has a low density (3.9 Mg/m³) and high structural lattice-gas-type occupational disorder (stronger than phasonic disorder). The superstructure, with 13-16% Co, stable between 500-850°C, is denser (4.1-4.2 Mg/m³) and presents lower occupational disorder. A little phasonic or orientational disorder [5,6] is evidenced by diffuse scattering. The superstructure modulation is clearly of chemical/occupational type, as in inequivalent average-structure unit cells the distribution of Al, Co, Ni atoms and vacancies between a common set of atomic sites is different. The higher local ordering is related to stronger Al-Co bonding interactions and lower temperature. An ordered Penrose-like tiling of atomic motifs (of larger size than in the average-structure) governs the atomic arrangement. Phason disorder is related to imperfect superordering of the larger structure motifs, as suggested by the FWHM trends observed for the different reflection classes.

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**VARIATION OF Q AND ITS RELATION TO THE STRUCTURAL
FEATURES IN Ca₂CoSi₂O₇**

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The incommensurate phase of Ca₂CoSi₂O₇, tetragonal, is stable between 242 and 489 K. The higher temperature phase is a non-modulated phase and the lower one is commensurate. The magnitude q , the component of the primary modulation wave-vector, varies continuously from 0.286 to 1/3 with temperature change. The incommensurate structure determined by a five-dimensional description indicates that the modulation is based on the shifts of Ca and O and the shifts induce variations of the coordination numbers of Ca atoms (from six to eight) in the structure. Four arrays of the six-coordinated Ca polyhedra form a bundle along the c -axis, and the distribution of the bundles at 468 K ($q=0.289$) is different from that at 297 K ($q=0.291$). Thus the present studies have been undertaken to characterize the distribution of the bundles corresponding to different q -values. The modulated structures with the q -values in the above range have been constructed using the method by which the atomic positions in the modulated structures are derived with the q -value and the modulation amplitudes of the atoms at 297 K. The structures of the incommensurate phase ($q=0.289$) and the orthorhombic commensurate phase were derived by the method and then successfully refined. This indicates that the variation of the ordering scheme of the bundles in the incommensurate and commensurate structures can be interpreted as the structures with systematic phase changes of the modulation waves at the section in the five-dimensional space, which corresponds to the three-dimensional space.

Keywords: Ca₂CoSi₂O₇ INCOMMENSURATE STRUCTURE PHASE
TRANSITION