

FA3-MS21-T01

Structural modulation in ferromagnetic shape memory martensitic phases. Lara Righi. *Dipartimento di Chimica GIAP, Università degli Studi di Parma, Parma, Italy.*

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Multifunctional ferromagnetic shape memory Heusler Ni-Mn-Ga alloys are frequently characterized by structural modulation in martensitic phases. In particular, modulated martensitic phases, showing the higher magnetic field induced strain performance, are the most promising candidates for technological applications. Depending on the composition, as well as pressure and temperature conditions, this periodic structural distortion, consisting of shuffling of atomic layers along defined crystallographic directions, accompanies the martensitic transformation. Over the years, different Ni-Mn-Ga modulated martensitic structures have been observed and classified depending upon the periodicity of corresponding ideal nM superstructure (where n indicates the number of basic unit cells constituting the superlattices). On the other hand, it has been demonstrated that in most cases such structural modulation is incommensurate and the crystal structure has been fully determined by applying superspace formalism [1,2]. The results, obtained by structure refinements on powder diffraction data, suggest a unified crystallographic description of the modulated martensitic structures, here presented, where every different “ nM ” periodicity can be straightforwardly represented.

[1] Righi L., Albertini F., Calestani G., Pareti L., Paoluzi A., Ritter C., Algarabel P.A., Morellon L., Ibarra M. R. *J. Solid State Chem.* 2006, 179, 3525. [2] Righi L., Albertini F., Villa E., Paoluzi A., Calestani G., V. Chernenko V., S. Besseghini S., C. Ritter C., F. Passaretti F., *Acta Mater.* 2008, 56, 4529.

Keywords: shape-memory alloys, martensitic alloys, incommensurate modulated structures

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Simulation of modulated reflections. Jeffrey J. Lovelace^a, Martyn D. Winn^b, Gloria E. O. Borgstahl^a.

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In a modulated crystal, the repeating unit is not periodic but contains a disorder of the molecules that can sometimes be described with a mathematical function. In the diffraction pattern from such a modulated crystal the standard periodic main reflections are flanked by satellite reflections. Generally, incommensurately modulated crystal diffraction cannot be simply described using integers along the reciprocal-lattice directions. However, in the special commensurate case where the satellite spacing is rational relative to the main reflections, a supercell can be used to describe the modulation. Using a supercell allows structural processing to proceed in a ‘normal’ fashion but with the downside of dealing with many more atoms. Not much is known about the relationship between a highly modulated macromolecular crystal and the resulting satellite intensities so in this study a modulated protein crystal

was simulated using a supercell approach. The protein superstructure was modulated to varying degrees and the resultant diffraction patterns and electron-density maps were studied to understand better how a modulation may manifest itself in real protein data. In the case that was evaluated, relatively small structural modulation resulted in significant satellite intensities. Interesting cases were observed where extinguished main reflections had strong satellites.

Keywords: incommensurate crystallography, modulated protein crystals, computer simulation

FA3-MS21-T03

Formation and stability of quasicrystals and other complex intermetallics. Walter Steurer. *Laboratory of Crystallography, ETH Zurich, Switzerland.*

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Already the early rapid solidification experiments on Al-Mn showed that quasicrystals (QC) can grow much faster than their approximants. This has been mainly attributed to the lower nucleation barrier of QC due to the local icosahedral order already present in the melt. However, this does not explain, how quasiperiodic long-range order can be established without much diffusion and why never high rational approximants are formed instead. What lets quasiperiodicity win over the periodic order of approximants? Certainly not the perfect regularity of icosahedral clusters that is possible in QC. The fundamental clusters are in both cases equally distorted, they are far from ideal icosahedral symmetry. Another open question is why the structures of QC are closer to ideal quasiperiodicity than to the averaged one of random tilings.

I will present models that offer answers to some of these questions. Beside other factors, particularly the role of clusters and flat atomic layers for the growth and stability of QC and other complex intermetallics will be discussed. An example is illustrated in Fig. 1, where the projected structures of an icosahedral QC, its 1/1-approximant and the largest known intermetallic structure are shown. It is obvious that all atoms of the QC are located on quasiperiodically spaced sets of flat atomic layers which obey the icosahedral symmetry. A completely different picture is obtained along the pseudo-5-fold direction of the 1/1-approximant although the local structures are similar. In this case the icosahedral symmetry of the clusters does no more coincide with the symmetry of the cubic approximant. It is also remarkable that all structures of intermetallics with periodic structures and giant unit cells show an analogue abundance of flat atomic layers what is already well known for Frank-Kasper phases. The interplay of cluster formation in a framework of atomic layers assists atoms to find their sites in unit cells with thousands of atoms.

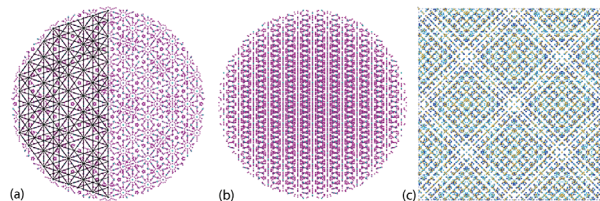


Fig. 1 Projections of the structures of (a) $i\text{-Cd}_{84}\text{Yb}_{16}$ along the 5-fold axis, (b) $1/1\text{-Cd}_6\text{Yb}$ along the pseudo-5-fold axis and (c) $cF(23,256-x)\text{-Al}_{55.4}\text{Cu}_{5.4}\text{Ta}_{39.1}$ along [100].

Keywords: intermetallics, quasicrystals, crystal growth mechanisms

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Photo-induced incommensurate ordering in an Fe(II) spin crossover complex. Sébastien Pillet,^a Chou-Fu Sheu,^b I-Jui Hsu,^b Vaclav Petricek,^c Michal Dusek,^c Claude Lecomte^a, Yu Wang^b. ^aCRM2, Nancy-Université, Vandœuvre lès Nancy, France. ^bDepartment of Chemistry, National Taiwan University, Taipei, Taiwan. ^cInstitute of Physics, Academy of Sciences of the Czech Republic, Praha, Czech Republic.
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Molecular multistability has attracted an increasing interest in the context of functional molecular materials. The possibility of switching between different stable states under external perturbation like temperature, pressure or light excitation allows to tune and control the macroscopic properties (magnetic, electronic, optic) of the system. In the solid state, strong coupling between purely molecular aspects and intermolecular interactions may lead to collective phenomena, i.e. photo-induced phase transitions [1]. Spin crossover (SCO) materials are typical examples of such photo-switchable molecular systems [2].

We investigate the laser light-induced switching process in the SCO complex $\{\text{Fe}(\text{abpt})_2[\text{N}(\text{CN})_2]_2\}$, through time and temperature dependent photo-crystallographic measurements. The crystal structure is built from the stacking of two different misfit 2D layers. Upon laser light excitation, an unprecedented collective long range ordering of the dicyanamide $[\text{N}(\text{CN})_2]$ groups develops, resulting in a displacive modulation of the crystal structure with wavevector \mathbf{q} , incommensurate with the underlying crystal lattice. The corresponding structural analysis of the metastable phase is performed under the superspace group approach, using JANA [3]. A lattice structural instability, resulting from competing interactions within the two layer subsystems, is evidenced as the basis for the disorder-to-incommensurate order phase transition.

[1] *Photoinduced Phase Transitions*, edited by K. Nasu (World Scientific, Singapore, 2004). [2] P. Gutlich and H. A. Goodwin (Eds), *Topics in Current Chemistry*, Vol. 233, 234, 235, Springer-Verlag, Berlin (2004). [3] V. Petricek and M. Dusek, JANA2000. Institute of Physics, Praha, Czech Republic (2000).

Keywords: phase transitions, incommensurate ordering, photochemistry

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Modification of modulated structures and nanodomains in $(A)_2\text{ZnCl}_4$ mixed crystals. Karsten Behrendt, Holger Gibhardt, Klaudia Hradil, Jeannis Leist, Götz Eckold. *Institute for Physical Chemistry, Georg-August-University Göttingen, Germany.*
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Rb_2ZnCl_4 and K_2ZnCl_4 belong to the family of A_2BX_4 -compounds that exhibit a variety of modulated structures. At low temperatures, a ferroelectric commensurate phase is stable which is transformed into the incommensurate structure on heating ($T_c = 192$ K for Rb_2ZnCl_4 and 403 K for K_2ZnCl_4).

Close to this lock-in transition, the incommensurate phase consists of an ordered sequence of polar nano-domains with alternating polarization. The characteristic variation of the modulation wavelength is associated with the motion and therefore creation/annihilation of domain walls. This mechanism is strongly influenced by defects that act as pinning centers.

In this contribution it is shown that chemical doping can be used to produce stable nano-domain systems even at room temperature. Using high-resolution γ -ray diffraction and neutron scattering with *in-situ* measuring of permittivity, we studied the variation of the modulated structure of doped $(\text{Rb}(\text{K}))_2\text{ZnCl}_4$ and $(\text{K}(\text{Rb}))_2\text{ZnCl}_4$ as well as changes in the phase transitions.

At small dopant concentrations, the lock-in already becomes rather diffuse with an extended coexistence regime and a pronounced thermal hysteresis. Such a gradual transition indicates the presence of various pinning centers of different strength. Under the influence of an applied electric field, the polar commensurate phase nonetheless is stabilized just as in the pure substances.

If, however, strongly doped systems are considered like $(\text{K}_{0.92}\text{Rb}_{0.08})\text{ZnCl}_4$, a coexistence of several disordered phases including the commensurate one is found in virgin crystals grown close to room temperature. Interestingly, they transform irreversibly on heating into a well-defined incommensurate phase that remains stable on subsequent cooling down to temperatures below 100 K. Pinning obviously becomes strong enough to completely suppress the lock-in transition. Third-order satellite reflections of high intensity can be observed, proving that the incommensurate phase consists of a regular array of polar nano-domains.

This structure then seems to be frozen and cannot be altered either by temperature changes or by the application of electric fields. Hence, $(\text{Rb}/\text{K})_2\text{ZnCl}_4$ provides a model system for self-assembled nanoscale anti-ferroelectric structures that can also be stable under ambient conditions thus facilitating further investigations, e.g. surface analysis.

Keywords: incommensurate modulated structures, domain structure, crystals in electric fields