Keywords: intermetallics, quasicrystals, crystal growth mechanisms

FA3-MS21-T04

Photo-induced incommensurate ordering in an Fe(II) spin crossover complex.

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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 $\{Fe(abpt)_2[N(CN)_2]_2\}$, 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 $[N(CN)_2]$ groups develops, resulting in a displacive modulation of the crystal structure with wavevector **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

FA3-MS21-T05

Modification of modulated structures and nanodomains in $(A)_2ZnCl_4$ mixed crystals.

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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 $(Rb(K))_2ZnCl_4$ and $(K(Rb))_2ZnCl_4$ 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 $(K_{0.92}Rb_{0.08})ZnCl_4$, 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, $(Rb/K)_2ZnCl_4$ 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