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High-pressure studies of organic molecular crystals

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Minerals, metals, inorganic materials, ices, gas hydrates and clathrates are "traditional" systems for high-pressure studies. On the other hand, high-pressure studies of complex biological systems, in particular, of proteins, are becoming more and more common. The effects of high pressure on organic molecular crystals were described in the early classical works by P. Bridgman and L. Vereshchagin, but these systems remained very little studied until the systematic work initiated by A. Katrusiak in the late 1970s, who has combined precise X-ray single-crystal diffraction studies, spectroscopy and calorimetry. In the last years, however, more and more research groups join the high-pressure studies of organic molecular crystals, and in this presentation I shall try to illustrate on several examples, mainly from my own experience, why these studies are so challenging and promising. In particular, I shall consider: the studies of the anisotropy of structural strain within the range of stability of the same polymorph as a tool to study intermolecular interactions, thermodynamic and kinetic aspects of pressure-induced phase transitions, comparison of the low-temperature and high-pressure behaviour, high-pressure studies of the polymorphism of drugs in relation to tableting procedure in industry, organic molecular crystals as biomimetics - high-pressure behaviour in relation to folding.

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- [1] Boldyreva, E.V. in *High-Pressure Crystallography*, Ed. Katrusiak, A. & McMillan, P.F. Kluwer, Dordrecht, 2004, 495.
- [2] Boldyreva, E.V. *J. Mol. Struct.* 2003, 647, 159.
- [3] Boldyreva, E.V. *Cryst. Engineering*, 2004, 6, 235.
- [4] Boldyreva, E.V. *J. Mol. Struct.*, 2004, 700, 151.
- [5] Boldyreva, E.V. *Russ. Chem. Bulletin*, 2004, 53, 1315.
- [6] Boldyreva, E.V. et al. *Arkivoc*, 2004, XII, 128.
- [7] Goryainov, S.V.; Boldyreva, E.V.; Kolesnik, E.N. *Chem. Phys. Letters*, 2006, 419, 496.

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Structural features related to pressure-induced electronic/magnetic phenomena in TM compounds

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The main issue of this paper is structural aspects of magnetic/electronic transitions in strongly correlated systems in a regime of very high static density. To achieve these objectives we carried out X-ray diffraction (XRD) measurements up to 120 GPa using diamond anvil cells to probe structural features specifically related to pressure-induced (PI) electronic/magnetic phenomena in transition metal compounds. The XRD data were analyzed taking into account the detailed results of (a) Mössbauer spectroscopy with its hyperfine interaction as magnetic probes (b) electrical resistivity as a tool to identify gapped or gapless states, and (b) Raman spectroscopy as an optical means for the study of subtle structural modifications. We concentrated on the following phenomena:

(i) Sluggish structural phase transition in antiferromagnetic insulator FeI₂ and ferrimagnetic semiconductor FeCr₂S₄ attributed to the onset of a Mott transition. The study of FeI₂ shows hints to Fe-positions disorder in addition to a reduction in volume. In the case of FeCr₂S₄ the Mott transition developing in the LP phase is accompanied by an appreciable volume decrease and gives rise to a first-order phase transition from spinel to Cr₃S₄-like structure.

These studies allow establishing features of the structural transformation specifically attributed to the MT for different types of the electronic transitions (Mott-Hubbard and Charge-Transfer).

(ii) P/I valence transformation in the layered antiferromagnetic Cu⁺¹Fe³⁺O₂ delafossite. This process results in part of Fe³⁺ converting into Fe²⁺ and has to be accompanied by Cu¹⁺ → Cu²⁺ partial transition with the creation of the new Cu²⁺ magnetic sublattice. XRD studies have shown structural phase transition corroborating with the discussed valence transformation. According to preliminary data analysis the new phase has similar to LP phase hexagonal layered structure but in contrast to the LP phase accommodates two different types of Fe and Cu sites.

(iii) P/I reversible charge transfer between octahedral (B) and tetrahedral cation (A) sites in the magnetite (Fe₃O₄) resulting into inverse- to normal spinel transition. It is shown that this transformation concurs with a significant increase of tetrahedra volume as a result of Fe³⁺ → Fe²⁺ transition on the A-sites, and with decrease of octahedral volume following Fe^{2.5+} → Fe³⁺ transition on the B-sites. On the basis of isobaric and isothermal measurements it was found the (P,T) phase boundary between the inverse, normal spinel and mixed-charge phases of magnetite.

(vi) Pressure-temperature driven Verwey transition in magnetite: the experimental documentation that Verwey transition temperature T_v(P) scales with the temperature of a reversible, cubic to a *distorted-cubic*, structural transition T_{DIST}(P). This implies that the pressure-temperature driven metal-insulator Verwey transition is caused by a gap opening in the electronic band structure due to the crystal-structural transformation to a lower-symmetry phase.