MS39 O1

Can superspace reinvent crystal chemistry?

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The superspace concept is currently applied with success for the determination and description of incommensurately modulated crystal structures (IMSs). The number of IMSs is increasing similar to the increase of the number of 3-dimensional (3D) structures starting from the sixties of last century. With the number and complexity of the determined 3D structures, crystal chemistry started to evolve in order to bring some better understanding in the manifold of structures. Three well known examples of the results of this development can be cited: (i) experimentally determined interatomic distances essentially improved, corrected and sometimes reversed both the *chemical bond* and the molecular structure concepts; (ii) the determination of the symmetry of crystal structures induced the development of the *phase transition* theory based on the group-subgroup relationships; (iii) the large manifold of crystal structure determinations generated the need to classify them. For instance, the concept of *structure type* (*ST*) was introduced for the investigation and prediction of both physical and chemical properties of compounds. It appears that the (3+*d*)D IMSs can be used for further development of the field of crystal chemistry. The basis of this development refers to the improvement and generalisation of fundamental crystal chemical approaches considering (3+*d*)D symmetry. The generalisation of the concepts relies on additional atomic characteristics varying in terms of additional internal dimensions. Experimentally determined interatomic distance variations allow to reveal both the interatomic interactions and the origin of the modulation in an IMS [1,2,3]. A single IMS of a compound with complex chemical composition presents a unique new opportunity to estimate the relative flexibility and rigidity of *chemical bonds* appearing between atoms [1,2,3]. The role of atomic interactions in the series of *phase transitions* can be also better understood if one of the phases is an IMS [4]. The experimentally determined variation of the atomic site occupancy in an IMS opens a new way for the description and prediction of order-disorder *phase transitions* [5]. With the example of scheelite-like family, it is shown that the concept of *ST* can be generalized in the frame of (3+*d*)D superspace groups of symmetry. A family of compounds can be represented as a family of 3D sections of a single (3+*d*)D IMS. This family can be defined as a (3+*d*) *ST*. The (3+*d*) *ST* definition encompasses the traditional *ST* but extends it in order to include also *ST*-like, *ST*-relative and IMSs. The determination of one IMS allows to fully describe the (3+*d*)D corresponding *ST* and to predict its members. The extension of crystal chemistry into (3+*d*)D superspace opens new perspectives in the field of condensed matter physics and other material sciences.

[1] Arakcheeva, A.; Chapuis, G.; Petříček, V.; Dušek, M.; Schönleber A. *Acta Cryst*. 2003, B59, 17.
[2] Chapuis, G.; Arakcheeva, A. *Z. Kristallogr*. 2004, 219, 730.
[3] Morozov, V.; Arakcheeva, A.; Chapuis, G.; Guiblin, N.; Rossell, M.; van Tendeloo, G. *Chem. Mat*. 2006, 18, 4075.
[4] Arakcheeva, A.; Chapuis, G. *Acta Cryst*. 2005, B61, 601.
[5] Arakcheeva, A.; Chapuis, G. *Acta Cryst*. 2006, B62, 52.

MS39 O2

New aspects in the analysis of compositionally flexible systems in the superspace: Fe_{1-x} S and Sb_{1-x} Te_x

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It has been proved in the recent literature with several examples [1,2] that the superspace formalism is a powerful tool to describe families of compounds of flexible composition using a single structural model. Typically these structures can be viewed as the stacking of a (few) different layers and the number and stacking of layers depend on composition. The atoms are represented in the superpace by atomic domains (AD). An essential feature of the superspace models for these families is the fulfillment by some ADs of the so-called *closeness condition*. This means that the lower limit of the projection onto the internal space of an AD coincides with the upper limit of the projection of another AD which is equivalent by a superspace unit cell translation. This yields, in general, real space configurations where the atomic motifs represented by these ADs are distributed within the layers as regularly as possible, producing so-called *uniform* sequences [3]. The application of the superpace description to the compounds $Sb_{2n}Te_3$ and $Fe_{1-x}S$ reveals new aspects of this approach.

Ab-initio calculations have been performed in idealized layer configurations of the pyrrhotite $Fe_{1-x}S$ [4]. For these configurations, Fe atoms are not located in equilibrium positions, and suffer a force directed to neighboring Fe vacant positions. These forces can be embedded in superspace showing a smooth variation within the ADs. This has been used to assess the relevant superspace symmetry. The $Sb_{2n}Te_3$ family, analyzed in [5], is different to the previous cases because the uniformly distributed motif is not a unique layer, but a block formed by 5 layers. This difference implies in superspace a “generalized” closeness condition where the ADs involved are separated by non-elementary superspace lattice translations.

[1] Elcoro L, Perez-Mato, J. M., Withers, R. L., Zeitschrift Fur Kristallographie, 2000, 727
[2] Elcoro L., Perez-Mato, J. M., Darriet, J., El Abed, A., Acta Cryst. 2003, 217
[3] Elcoro, L., Perez-Mato, J. M., Withers, R. L. Acta Cryst. 2001, 471–484.
[4] Izaola, Z., González, S., Elcoro, L., Perez-Mato, J. M., Madariaga, G., García, A.. *Acta Cryst*. submitted
[5] Kifune, K., Kubota, Y., Matsunaga, T., Yamada, N.. *Acta Cryst,* 2005, 492.