In recent years, a constant attention has been focused onto copper in low dimensional structural environments showing an aperiodic character and related to interesting physical properties (high Tc superconductors, spin ladder compounds). Recently, a new composite structure was isolated in the Ca-Cu-O system. The structure of the Ca(Cu1/2Co1/2O5) compound, determined by single crystal X-ray diffraction using the 4-D formalism [1,2] corresponds to two interpenetrating orthorhombic F sublattices, exhibiting incommensurate periods along the [100] direction. The two subsystems are respectively constituted of 1-D infinite [MO2] chains (M = Cu or Co) and of Ca layers. This structure is closely related to oxide structures already depicted [3], but the 4-D composite description gives a new interpretation of the Ca/(Cu+Co) ratio in the above formula. The actual symmetry of this structure class is now proved to be rigorously described in the superspace formalism. The modulation functions have been refined and allow a spectacular distance accommodation between the two sublattices. Moreover, the structure refinement shows that a substitution of Co for Cu in this type of compound is possible, which could be compatible with a charge localization of the type Cu2+, Co3+.

References

Keywords: APERIODIC STRUCTURE COPPER OXIDE 4D REFINEMENT

The structure of a multiple-domain crystal of $\text{YV}_4\text{O}_8$ was refined on the assumption that α-form, β-form and their respective twin forms intergrow mutually. The model was expressed as a commensurate composite crystal with two kinds of subsystems, one is $\text{V}_4\text{O}_8$ part and the other is Y part, and refinement was performed using high-dimensional formalism and all reflections from all domains simultaneously. Next, diffuse streaks observed in the X-ray and electron diffraction patterns were simulated using the matrix method which has been used for one-directional disorder such as stacking faults.

Keywords: COMPOSITE CRYSTAL, DIFFUSE SCATTERING, PHASE TRANSITION

The 4,4'-Diethoxyazobenzene ($\text{C}_8\text{H}_8\text{N}_2\text{O}_3$) presents two distinct solid state phases by cooling from the melting point around 403 K down to 100 K. Phase transition takes place at 356 K leading to a triclinic structure, space group $\text{C}$1, stable above 356 K, is modulated [1]. Its average structure was initially described in the monoclinic space groups $\text{P}2_1\text{I}$, stable above 356 K, is modulated [1], but the 4-D composite description gives a new interpretation of the Cu/Cu-Co ratio in the above formula. The actual symmetry of this structure class is now proved to be rigorously described in the superspace formalism. The modulation functions have been refined and allow a spectacular distance accommodation between the two sublattices. Moreover, the structure refinement shows that a substitution of Co for Cu in this type of compound is possible, which could be compatible with a charge localization of the type Cu$^{2+}$, Co$^{3+}$.

References

Keywords: ORGANIC COMPOUNDS, MODULATION, DISORDER

Models used for refinement of modulated structures are usually presented as sets of Fourier coefficients describing the occupation probabilities or displacement vectors of particular atoms(molecules). The use of symmetry is restricted to imposing extra constraints for symmetry equivalent atoms. However the same model can be described using smaller number of parameters. The essential fact is that structural phase transitions usually take place according to one or more irreducible representations of the high symmetry space group. Such a property allows calculation of the symmetry reduction model and the respective atomic translations or occupation probabilities. Practical implementation of the above procedure can be found in MODY program, written by W.Sikora and P.Czapnik, calculating the basis functions for a given representation. The calculated basis functions exhibit some interesting features: as a rule they are orthogonal and they contain only a limited number of parameters which describe the structure on all atomic sites. As the basis functions are usually complex an additional restriction is imposed: the coefficients of the linear combination of basis functions should be selected in such a way that the resulting structure model (displacements or probabilities) has to be real. The respective system of equations of equations can be reduced to a linearly independent set and then solved for the unknown coefficients. After such operation the final structure model contains clearly defined minimum number of free parameters, which can be easily transformed to the equivalent set of Fourier coefficients. Examples will be given for some typical cases.

Keywords: STRUCTURE REFINEMENT SYMMETRY