MS24-P4 Interpretation of single crystal diffuse scattering augmented by density functional theory and spectroscopy

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Ever since the pioneering works of the Braggs which started crystallography and Born and von Karman which started the field of vibrational spectroscopy, the two disciplines were seen as being separate.

Borns insight into the nature of thermal diffuse scattering (TDS) arising in crystallographic experiments established a link between the two [1]. When using X-ray diffraction, the TDS is integrated in energy but resolved in momentum. Interesting effects can occur in a time-of-flight single crystal neutron diffraction experiment, when some neutrons can accidentally match the wave-vector and energy of phonons, as has been noted by Willis [2].

The complementarity of using spectroscopy, TDS and density functional theory will be illustrated in a series of Alanine compounds.

In addition, we have devised a method of simulating the diffuse scattering arising from one-phonon inelastic excitations in a neutron time-of-flight Laue single crystal experiment. These effects are illustrated experimentally using NaCl, the first crystal structure solved by the Braggs. In addition they are simulated using DFPT phonons obtained from CASTEP first principles code.

[1] M. Born and K. Lonsdale, Nature 150, 490 (1942).

[2] B. T. M. Willis, Acta Cryst. A42, 514 (1986).

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MS24-P5 Disordered structure of the Mg-Al and Ni-Al oxides prepared by the thermal decomposition of layered double hydroxides

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The structures of the mixed oxides prepared by the decomposition of Mg-Al and Ni-Al layered double hydroxides (LDH) at the moderate temperatures (400 – 800 ^{o}C) have not been completely investigated up to now. It is related with the presence of a diffuse scattering along with the peaks inherent to MgO- or NiO-like structure on the XRD patterns. The HRTEM evidences that the structures of the mixed oxides are different. The Mg-Al oxide structure is disordered in three directions. The Ni-Al oxide has the 1D disordered sandwich-like structure. These data were used for the simulation of the XRD patterns on the base of the models of 1D and 3D disordered crystals with use of the DIFFaX software and the self-developed Debye equation scattering program.

By means of the Debye simulation it was confirmed that structure of the Mg-Al oxide is very defective and consists of the layers of octahedrally (O) coordinated cations as in the MgO structure in [111] direction and mixed octahedral-tetrahedral (OT) layers as in a spinel structure. Layers contain row-ordered cation vacancies. On the Figure one can see that the presence of the OT layers results in decrease in the intensity of the 200 diffraction peak of MgO-like structure and appearance of the two peaks of diffuse scattering. Ordering of cation vacancies leads to the stacking faults (SFs) in the plane of layers that broadens the first peak of diffuse scattering. At the definite concentrations of defects a good correspondence between the experimental and calculated XRD patterns is achieved.

Such disordered structure can be formed as a result of a migration of Al^{3+} ions from LDH's Mg-Al brucite-like layers to the interlayer during thermal removing of water molecules, hydroxyl- and carbonate-ions. Reconstruction of the LDH's hydrotalcite structure from the mixed Mg-Al oxide upon contact with water can be explained by the reverse migration of cations during the filling of interlayers by water and hydroxyl-ions. This model is not suitable for the non-rehydratable Ni-Al oxide. It was shown that the one part of Al^{3+} ions keeps in octahedral layers and the other part migrates to the surface forming amorphous alumina. By means of the simulation it was shown that possible presence of spinel-like surface layers epitaxially connected with NiO-like core can lead to the appearance of the diffuse scattering observed on the experimental XRD patterns.

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