

Structure determination of intermetallic compounds using electron crystallography methods

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Structure and properties of materials are intimately linked, thus study of crystal structure of novel materials is crucial for fundamental understanding of their properties. When single crystals of sufficient size are available, single crystal X-ray diffractometry is used for the solution of the structure. If unknown phase cannot be obtained as single crystal, its structure should be solved by other methods, such as X-ray powder diffraction or electron crystallography. Since nowadays majority of crystals of the interest became smaller in size – powder X-ray diffractometry cannot be used for solution of their atomic structure, mainly due to the effect of peak broadening. Electron crystallography emerges as important and sometimes the only possible tool for structure determination of nano-sized crystals.

The first step of crystal structure determination by electron crystallography consists of analysis of electron diffraction patterns (conventional selected area and/or convergent beam patterns including high order Laue zones) for deducing the unit cell parameters of the unknown structure and describing its symmetry by a proper space group [1]. The next step regards developing and verification of the structural model which can be done using various methods such as direct methods, charge flipping, simulated annealing, global optimization etc'. This chapter will underline one of many possible approaches which bases on combination of two techniques: a) direct methods, relying on the analysis of the measured kinematical (or close to kinematical) intensities of diffracted beams; and b) crystallographic image processing of HRTEM images, leading to determination of coordinates of heavy atoms.

Despite sustained effort over many years, the use of electron crystallography is still limited due to the problems arising from the dynamical nature of electron scattering. This means that intensities of electron diffraction reflections vary in a complex way with the thickness of the sample and, therefore, the diffraction intensities are not kinematical and cannot be taken as input data for direct methods.

Newly developed method of Precession Electron Diffraction (PED) [2-4] can be considered as promising technique for reducing the dynamical effects. Although in precession experiments the multi-beam effect still remains, the diffraction intensities are averaged due to integration through all directions within Bragg reflection width and, as a result, have pseudo-kinematical character. Another important feature of precession technique is related to the fact that the number of reflections associated with the high order diffraction Laue zones in precession patterns is much larger than that in Laue zones appearing in conventional electron diffraction. This allows collection of more reflections in high-order Laue zones. Thus PED pattern has larger resolution than regular selected area electron diffraction pattern and more kinematical intensities, so it was suggested that PED intensities can be used for structure solution of new materials. Following this idea, several structures of zeolites, complex oxides and minerals were solved using PED technique. Until today structure of intermetallic compounds was never solved fully (including atomic positions) using solely electron crystallography methods. It must be noted that strategies for structure solution of intermetallides should be different from those of zeolites and complex oxides, since

for intermetallics no strict constraints on coordination polyhedra, interatomic distances and angles can be applied.

Our flagship project deals with structure solution of novel intermetallic phases using electron crystallography methods. For this purpose we have been studying new ternary intermetallics found in ternary Al-T₁-T₂ systems (where T₁=Fe, Rh, Cu and T₂=Ru, Ir, Re, U, Th) [5-12]. Although some of the structures were solved using a combination of electron crystallography and powder X-ray diffraction methods – the aim of our research to develop strategies in order to be able to solve the structure (including finding the atom positions) using solely electron crystallography methods. Successful structure solution was already performed on known Mg₁₇Al₁₂ (β) phase used as case-study, whose structure was solved using PED data and developed strategies used for structure determination of new Al-Mg-Ag compound. As an example, Fig. 1 shows PED images that enabled space group determination of Al-Mg-Ag compound. Data extracted from three upper PED patterns allowed finding of 108 out of 152 atom positions, which is major leap forward for electron crystallography as a science.

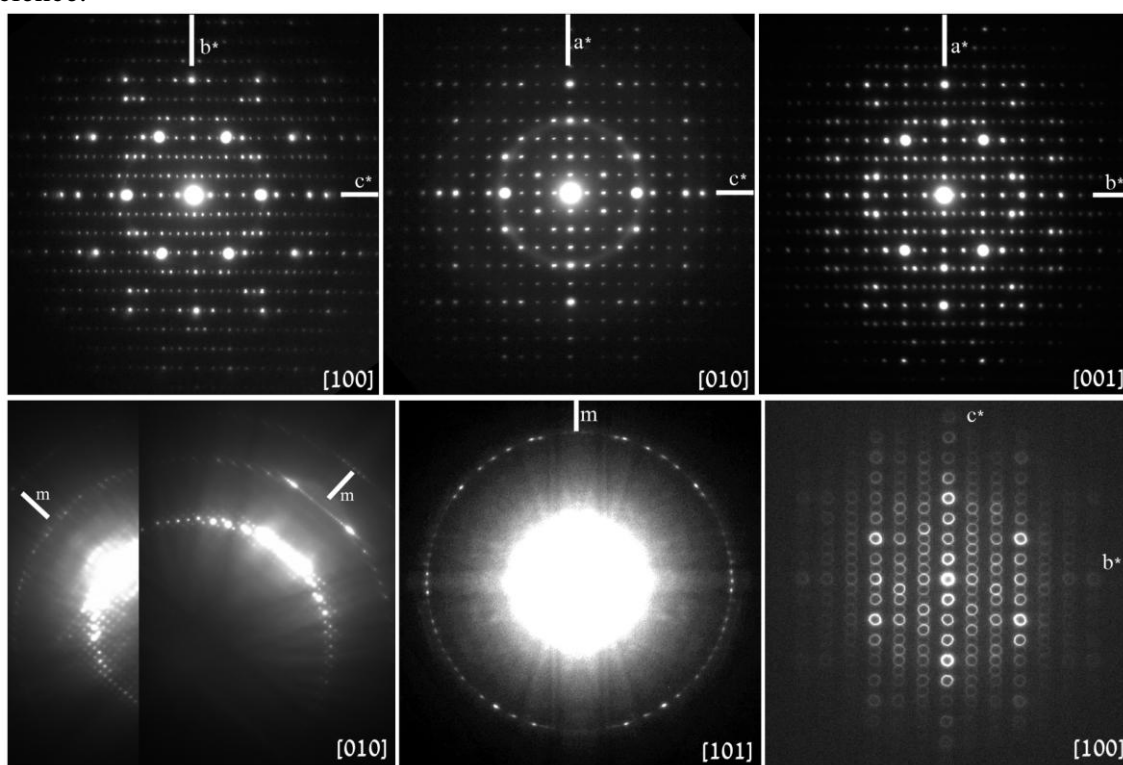


Fig. 1: upper row: PED patterns taken along [100], [010] and [001] orientation from new Al-Mg-Ag compound. Bottom row: [010] off-axis microdiffraction pattern, [101] microdiffraction pattern and [100] descanned PED pattern.

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