

Phonons in Demixing Systems

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Phonons reflect most directly the chemical interactions in solids. Hence, time-resolved lattice-dynamical experiments yield detailed information about the trajectories and mechanisms of solid state reactions.

Using the example of demixing-processes in the model-systems of silver-alkali halides we were able to demonstrate that the phase separation is a two stage process. While stroboscopic inelastic neutron scattering from phonons unambiguously prove that chemical demixing in the spinodal regime takes place on a time-scale of seconds, the relaxation of the lattice as reflected by the structural Bragg reflexions is a subsequent step on much longer temperature dependent time scale of hours, days or even months [1-4].

A reasonable way to overcome the problem of relatively low fluxes on neutron research reactors is to establish the stroboscopic method. Hence a reproducible cycling of temperature between the homogeneous state at 350 °C and the ageing temperature at 100 °C is required to scrutinize the demixing process in these model substance like silver alkali halides. This includes exact temperature profiles as well as the stability of the single-crystals over a total cycling time in the order of days. Temperature jumps from high to low temperatures were achieved in approximately 50 seconds, whereas time resolution steps lay in the order of one second.

While previous real-time investigations were focussed on acoustic phonons, we have now extended our experiments to optical phonons that are particularly sensitive to the local structure. Lattice dynamical model calculations allow us to provide a microscopic interpretation of the experimental results. Additional phonon modes observed in the homogeneous phase can be interpreted on the basis of locally ordered structure. This seems to be different from the findings in metallic alloys, where usually broad phonon spectra are observed, rather than well defined local modes. The possible reason for the different behaviour of binary salts is the almost rigid frame of the anion sublattice that remains invariant during demixing and homogenization.

Of particular interest is the time-evolution of phonon life times. It will be demonstrated that these depend strongly on the overall composition of the sample. Minority phases that are formed during the initial stage of decomposition exhibit large phonon line widths due to the small spatial extend. Thus surface effects disturb the prolongation of lattice vibrations. Only if the precipitates grow beyond some critical size by coarsening effects, the width of phonon spectra is drastically reduced. Using the information of time resolved small angle scattering experiments, it is possible to estimate the precipi-

tation size depending on the concentration of the silver alkali halide systems. This coarsening effect correlates with the evolution of the Bragg reflexions.

References

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