Thermal diffuse scattering from nanocrystalline systems

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The thermal diffuse scattering (TDS) in X-ray diffraction (XRD) patterns contains significant information about the local lattice dynamic structure of nanocrystalline systems [1]. Techniques such as the pair distribution function (PDF) are commonly employed to extract this information, where the correlated movement of atomic pairs is reflected by the breadths of the PDF peaks [2]. However, PDF techniques require a prior knowledge of phase composition for the Fourier transformation of the experimental XRD data, orientationally averaging the local dynamic information, rendering it not readily distinguishable from the static component. Herein, we explore the possibility of an analysis of local lattice dynamics based directly on XRD powder pattern modelling, where TDS is added to the structural model of the traditional Rietveld method [3] following the procedures developed by the authors for TOPAS in Ref. [4]. In conjunction with the whole powder pattern modelling approach [5], the crystallite shape and static components are simultaneously estimated. Two study cases of Pd nanocrystalline systems are analysed: (i) *in silico* nanosphere powder simulations via molecular dynamics (MD) and (ii) synchrotron radiation XRD powder patterns of Pd nanocubes. *In silico* analysis points out that the TDS model provides the correct trends of the correlated atomic movement up to the ninth coordination shell. The experimental case shows that this TDS model correctly estimates the force mechanisms of the nanocrystalline Pd system. The approach is also extended to binary materials such as Ag_2O [6], with data collected using synchrotron radiation at room temperature, supplemented by laboratory experiments up to 200°C. An Einstein model was used to derive the harmonic and anharmonic force constants of the system. The force constants were also obtained via density functional theory and *ab initio* molecular dynamics simulations and showed similar values to the experiments. The analysis reveals the complex dynamic structure of Ag_2O, characterized by high anisotropy in phonon dispersion relations and the presence of soft phonon modes, which explain the significant displacement parameters observed. The proposed approach can be employed for other binary or more complex systems to understand the dynamics of local forces through X-ray diffraction analysis, with appropriate tools developed to facilitate this implementation.

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