Treatment of disorder effects in X-ray absorption spectra by reverse Monte Carlo simulations: $CuMoO_4$ case

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Copper molybdate ($CuMoO_4$) is a thermochromic and piezochromic material, which exhibits structural phase transitions under the influence of pressure and/or temperature that make this material perspective in chromic-related applications starting from the user-friendly temperature and pressure indicators to "smart" inorganic pigments.

Since the functional properties of $CuMoO_4$ are directly connected with its local structure, X-ray absorption spectroscopy (XAS) is an obvious choice to probe structural changes during temperature variation including the phase transition. However, the interpretation of extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectra is not straightforward and often requires the use of advanced simulation tools. Treatment of thermal fluctuations and static disorder in XAS is a complex task, which can be successfully addressed by the reverse Monte Carlo (RMC) method [1, 2].

In this study, we used XAS at the Cu and Mo K-edges to probe the temperature-induced evolution of the local structure of $CuMoO_4$ in the range from 10 to 973 K (Fig. 1). At low temperatures, the thermochromic phase transition between α-$CuMoO_4$ and γ-$CuMoO_4$ with a hysteretic behaviour was observed [3] while at temperatures above 400 K, the thermochromic properties of α-$CuMoO_4$ were related to temperature-induced changes in the $O^{2-} \rightarrow Cu^{2+}$ charge transfer processes [4].

The structural information encoded in the EXAFS spectra was extracted by RMC simulations based on an evolutionary algorithm (EA) implemented in the EvAX code [1]. This method allows one to obtain a structural model of such complex material as copper molybdate accounting for multiple-scattering effects as well as structural and thermal disorder contributions in the experimental EXAFS data. The structural models obtained by RMC were used to simulate the Cu K-edge XANES spectra at a high-temperature range, in which the temperature effect is the most pronounced. The simulated XANES spectra are in good agreement with the experiment and reproduce the main temperature-dependent XANES features.

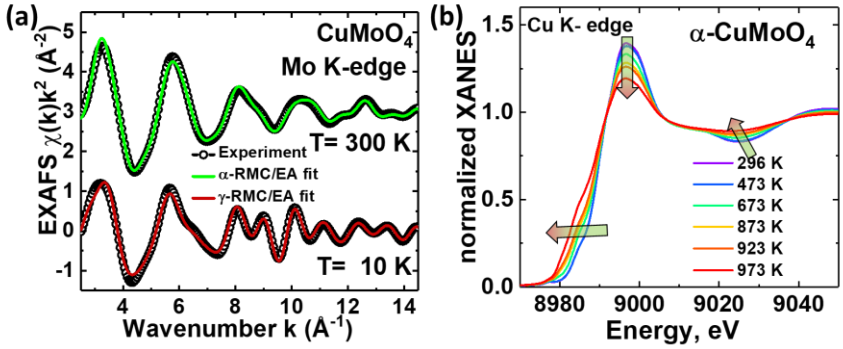

Figure 1. (a) Results of RMC/EA calculations for the Mo K-edge in $CuMoO_4$ at 10 and 300 K. (b) Temperature-dependent experimental Cu K-edge XANES spectra in the high-temperature range.

[1] J. Timoshenko, A. Kuzmin, and J Purans, (2014) *J. Phys.: Condens. Matter* **26**, 055401.

[2] I. Jonane, A. Anspoks, and A. Kuzmin, (2018) *Model. Simul. Mater. Sci. Eng.* **26**, 025004.

[3] I. Jonane, A. Cintins, A. Kalinko, R. Chernikov, and A. Kuzmin, (2020) *Rad. Phys. Chem.* **175**, 108411.

[4] I. Jonane, A. Anspoks, G. Aquilanti, and A. Kuzmin, (2019) *Acta Mater.* **179**, 1901132.

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