



Buckled crystalline structure of disordered mixed salts

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Abstract

Mixed salts $\text{AgBr}_{0.6}\text{Cl}_{0.4}$ and their pure components were investigated by XAFS. The concentration of the mixture was chosen to produce the homogeneous phase. Detailed analysis of the Ag and Br K edge data revealed an angular deviation of bonds in the mixture from collinearity. The corresponding RMS buckling angles ($11 \pm 2^\circ$) were determined using the strong angular dependence of the forward scattering amplitude in double- and triple-scattering focusing paths. The XAFS results were used to perform molecular-dynamics simulations which allowed to visualize the actual structure of the mixture.

Disordered system $\text{AgBr}_{0.6}\text{Cl}_{0.4}$ and the pure components AgBr and AgCl were investigated by means of the multiple-scattering (MS) XAFS analysis at the temperature 15 K. The pure salts were mixed in the concentration of their congruent melting, to ensure the homogeneity of their solid solution. It was shown that the local structure of this system deviates from the average NaCl one, in accordance with our previous results obtained for mixed alkali halides [1]. We demonstrated that atoms in the mixture formed stable configurations, buckled around the perfect lattice. To describe the deviations from the average structure we determined the buckling angles between the two adjacent bonds which are collinear in pure salts.

The mixed salts samples, initially prepared by the Bridgman–Stockbarger technique, were then pressed to the thickness x of 20–40 μm to satisfy the condition $\Delta\mu x \leq 1$ on the corresponding (Ag or Br) K edges. The pure salts were prepared from the high purity powders of raw materials. The XAFS measurements were performed on the beamline X11A at the NSLS with a double-crystal (111) Si monochromator. To extract the atomic back-

ground the computer code AUTOBK [2] (University of Washington) was used. The resultant $\chi(k)$, where k is the photoelectron wave number, was normalized to the K-edge jump.

To analyze the XAFS data we used the non-linear fitting method and computer code FEFFIT (University of Washington). The fit was performed in r space. The theory was calculated with the computer code FEFF5 [3]. Pure salts were analyzed within 8–9 Å around the central atom. It was found that the paths containing the first nearest neighbor (1NN) as the focusing atom (both double-scattering (DS) and triple-scattering (TS) paths) are enhanced compared to the single-scattering (SS) paths with the same path lengths. The mixture $\text{AgBr}_{0.6}\text{Cl}_{0.4}$ was analyzed using the same types of paths found important for the analysis of the pure salts. The check of the homogeneity of the solid solution was performed by fitting to the randomized atom Br XAFS data the FEFF5 theory combined from the Br–Ag(1), Br–Br(2) and Br–Cl(2) SS paths. Numbers in parentheses indicate the coordination shell. The paths to the 2NN were weighted with the composition x which was varied in the fit. Fit results showed that x agreed with the initial concentration of AgBr in the mixture within the

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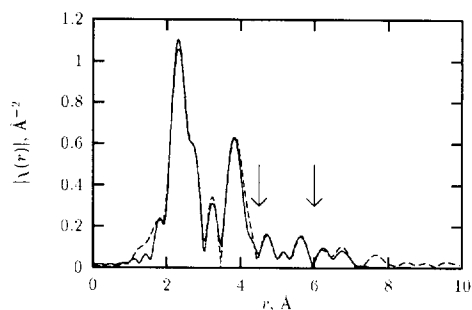


Fig. 1. Fourier transform magnitude of the Ag K-edge data (dash) and fit (solid) to the $\text{AgBr}_{0.6}\text{Cl}_{0.4}$.

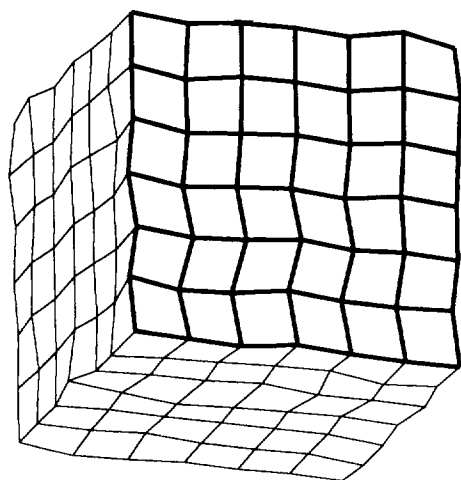


Fig. 2. Buckled structure of the $\text{AgBr}_{0.6}\text{Cl}_{0.4}$.

experimental uncertainty 2%, thus attesting to the homogeneity of the mixture.

To analyze the common atom (Ag) XAFS data we combined the total theoretical XAFS signal from the individual paths calculated with FEFF5 for the pure salts and weighted with composition. To account for the structure changes that occur in the mixture we varied the ΔE_i shift of the energy origin (different for different paths containing the 1NN [1]), σ_i^2 – Debye–Waller factors, ΔR_i – corrections to the half path lengths, and $\langle \Theta_i \rangle$ – RMS buckling angles of the Ag–Br–Ag and Ag–Cl–Ag bonds. To find $\langle \Theta_i \rangle$ we, first, calculated three reference paths to the 4NN buckled by 0° , 4° and 16° with FEFF5 and then determined the actual angles in the unknown data by a fit using a 3-point interpolation scheme. Our fit results are shown in Fig. 1. The r -range where the buckling angles are important is shown by arrows. The RMS angles for the Ag–Br–Ag and Ag–Cl–Ag bonds were obtained to be

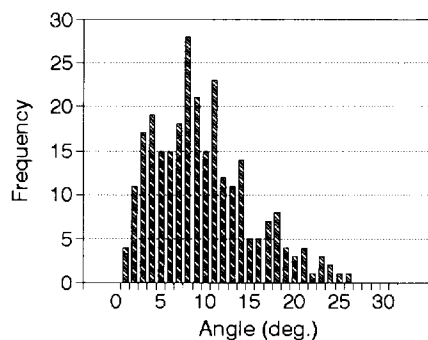


Fig. 3. Frequency distribution of the Ag–Br–Ag bond angles.

$10.7 \pm 2.0^\circ$ and $11.8 \pm 2.0^\circ$, respectively. Estimations gave the values of 2.5° for the angles due to thermal vibrations, thus the buckling we found is caused by a static rather than dynamic disorder.

To visualize the actual structure of the $\text{AgBr}_{0.6}\text{Cl}_{0.4}$ we used the molecular-dynamics code CLUSTER [1]. The interatomic potentials were considered harmonic. The force constants and equilibrium bond lengths were taken from our XAFS results. Simulation results gave an excellent agreement with XAFS analysis. The equilibrium bond lengths were consistent with those determined by XAFS within the 0.01 \AA uncertainty; buckling angles for the Ag–Br–Ag and Ag–Cl–Ag were equal to 10.1° and 10.6° , respectively. The buckled structure produced by the simulation is shown in Fig. 2. This picture should be considered as the actual structure of our mixed salt.

It is well known that the dielectric, optical, electrical as well as mechanical properties of single phase mixed salts depend on the character of the distortion of the perfect structure. The results we obtained inspire us to connect the properties of mixed salts to the properties of spin (or dipole) glasses. Indeed, any two adjacent distorted bonds which were collinear in the pure salts structures can be now associated with an effective *dipole* (or *spin*). While the average lattice is periodic, the distribution of spins orientations is random and frozen at low temperature. To study how the angles deviate from the average value we calculated the frequency distribution of the Ag–Br–Ag bond angles (Fig. 3). Since most angles exceed the zero motion vibrational angles of 2.5° , the effect of vibrations on the actual distribution is negligible.

This new approach may result in the generalization of the description methods of many kinds of mixed systems (not only ionic salts).

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