Measurement of local disorder and lattice vibrations is of great importance for understanding the mechanisms whereby thermoelectric materials efficiently convert heat to electricity. Calcium cobalt oxides (Ca2CoO3)0.62CoO2 is a model system in this regard with a figure of merit ZT above one. The compound has a complex misfit layered structure with significant lattice displacement (both static and dynamic) that is attributed to the reduced thermal conductivity. Its averaged structure consists of two interpenetrating subsystems of a CdI2-type CoO2 layer and a distorted tri-layered rock-salt-type Ca2CoO3 block (Fig.1,2), being incommensurately modulated along the b-axis. It is well known that both static displacement and thermal atomic vibration can effectively scatter phonons to reduce thermal conductivity, however, the exact scattering mechanisms are still unknown, largely because there is no reliable method available for such a measurement that can link the displacement to the phonon scattering.

Here, we demonstrate that the quantitative acquisition of multiple annular-dark-field images via STEM at different scattering-angles simultaneously (Fig.1) allows us not only to separate but also accurately determine static and thermal atomic displacement in crystals. This is because the intensity characteristics of a STEM image acquired with high angle annular dark field (HAADF) and medium angle annular dark field (MAADF) differ considerably, depending on the nature of the displacement (Fig.2a-b). Unlike diffraction analysis that derives the overall displacement from the intensities of Bragg reflections, we directly measure the atomic displacement in real space, thereby enabling us to refine independently the atomic displacement in the same lattice planes, i.e., in the rigid CoO2 and soft Ca2CoO3 layers (Fig.3), that is crucial to revealing their different nature in phonon scattering.

Applying our unique method to the layered thermoelectric material (Ca2CoO3)0.62CoO2 disclosed the presence of large incommensurate displacive modulation and enhanced local vibration of atoms, largely confined within its Ca2CoO3 sublayers. Relating the refined disorder to ab-initio calculations of scattering rates is a tremendous challenge. Based on our approximate calculation of scattering rates, we suggest that this well-defined deterministic disorder engenders static displacement-induced scattering and vibrational induced resonance scattering of phonons as the origin of the phonon glass (Fig.4). Concurrently, the crystalline CoO2 sublayers provide pathways for highly conducting electrons and large thermal voltages [1].


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Fig. 1: (a) Simultaneous acquisition of HAADF (114-608 mrad, b, d) and MAADF (46-104 mrad, c, e) images to determine the static displacement and atomic vibration in the [001] projection (b, c) and the [010] projection (d, e) of (Ca$_2$CoO$_3$)$_{0.62}$CoO$_2$. The embedded are simulated images.

Fig. 2: Bottom: Image intensity vs displacement. Calculated intensities (dashed) in the CoO$_2$ and CoO layers and intensity ratios I$_{CoO}$/I$_{CoO_2}$(solid) for HAADF (collection angle: 114 - 608 mrad) and MAADF (46-104 mrad) as function of (a) thermal mean-square displacement in the CoO layer, and (b) static displacement calculated as two cosine components, A$_1x$ & A$_2x$.

Fig. 3: Determining static- & thermal-displacement (a to d) simultaneous STEM images in[010]. Left: HAADF and Right: MAADF. (a) Experimental image; Calculated images with unrelaxed (b), and relaxed model (c) and our refined structure (d). (e) Intensity profiles. Open circles, green-, blue-, and red-lines are from (a), (b), (c), and (d), respectively.

Fig. 4: (a) Thermal conductivity vs temperature: circles are experimental data for (Ca$_2$CoO$_3$)$_{0.62}$CoO$_2$ and MgO. Solid lines are fitting from specific heat, DOS, group velocity, and MFP. Blue and red lines contain the Umklapp and Rayleigh terms, while the black line including the displacement and resonance terms. (b) MFP. (c-d) Phonon scattering mechanisms.