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Anisotropic heat conduction in the metal organic framework perovskites $[C(NH_2)_3]X(HCOO)_3$ ($X = Cu, Zn$)

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ABSTRACT

We report thermal conductivity (κ) measurements on single crystals of the metal-organic framework perovskite compounds $[C(NH_2)_3]X(HCOO)_3$ ($X = Cu, Zn$) in the temperature range $5\,K \le T \le 300\,K$. The directionality of N-H· · ·O bonds and their stretching due to the Jahn-Teller distortion in the Cu compound are identified as mechanisms underlying differences in the $\kappa(T)$ behavior for the two compounds and their anisotropy. For heat flow along a direction preferentially transverse to the N-H···O bonds, $\kappa \sim 0.6$ W/mK near 300 K, approaching the theoretical minimum value. A possible magnetic contribution to the heat flow in the Cu compound is also discussed.

Hybrid organic-inorganic perovskite compounds (HOIPs) of the form ABX_3, in which the A-site and/or X-site ions are organic amine cations and/or organic linkers, respectively, have attracted considerable attention for their promise in photovoltaic, optoelectronic, and thermoelectric applications.[1,2] A subclass of HOIPs having metal-organic BX_3 frameworks (MOFs) also possess novel and potentially useful properties, including ferroelectricity, magnetism, and multiferroicity.[1,3,4] These compounds offer promising opportunities for tuning the material properties and developing new functionalities because of their structural flexibility and chemical variability.

Mechanical properties and heat transfer play important roles in many applications, and both are dictated by the low-energy vibrations of materials. The A-site molecules in HOIPs introduce a range of soft intermolecular forces (e.g., from hydrogen bonds) which result in a high density of states in the phonon energy spectrum at low energy.[5,6] A very low thermal conductivity of halide-based HOIPs[7–10] has motivated interest in their potential use in thermoelectric energy conversion. Recent studies implicate the coupling of the A-site molecules to collective motions of the framework as a mechanism for such low values of the thermal conductivity.[11] The thermal conductivities of MOF perovskites are largely unexplored.[12] Of particular interest are several formate-based compounds that exhibit low-dimensional magnetism and multiferroicity.[3] These materials present the additional prospect of heat conduction via magnetic excitations[13,14] and tunable heat conduction in applied electric or magnetic fields.

Here, we report temperature-dependent thermal conductivity (κ) measurements on single crystals of the MOF perovskites $[C(NH_2)_3]Cu(HCOO)_3$ (1-Cu) and their nonmagnetic analogue $[C(NH_2)_3]Zn(HCOO)_3$ (2-Zn). These compounds have $A = C(NH_2)_3^+$ (guanidinium), $B = Cu^{2+}$ or Zn^{2+}, and $X = HCOO^-$ (formate), with an orthorhombic crystal structure (space groups $Pna2_1$ for 1-Cu and $Pnna$ for 2-Zn).[3] The corners of the BO_6 octahedra for both compounds are bridged by formate molecules to form the metal-formate framework[15] (Fig. 1). For 1-Cu, Jahn-Teller distorted CuO_6 octahedra possess four short and two elongated Cu-O bonds. Its framework comprises antiferromagnetic (AF) coupled chains [Fig. 1(a)] of Cu^{2+} spins involving short Cu-$O_{formate}$ bonds (along the crystallographic *c* axis), with substantially weaker ferromagnetic coupling between chains dictated by the elongated bonds. Orbital ordering within the *ab* planes is evidenced by an antiferro-distortive pattern of elongated and short bonds.[16] The magnetic and orbital structure is quite similar to that of $KCuF_3$,[17,18] and the long-range AF spin order occurring below $T_N \simeq 4.6$ K is thus expected to be of A type.

We find that both the temperature dependence and anisotropy of the lattice thermal conductivity for both compounds are strongly influenced by the directionality of N-H···O bonds connecting the

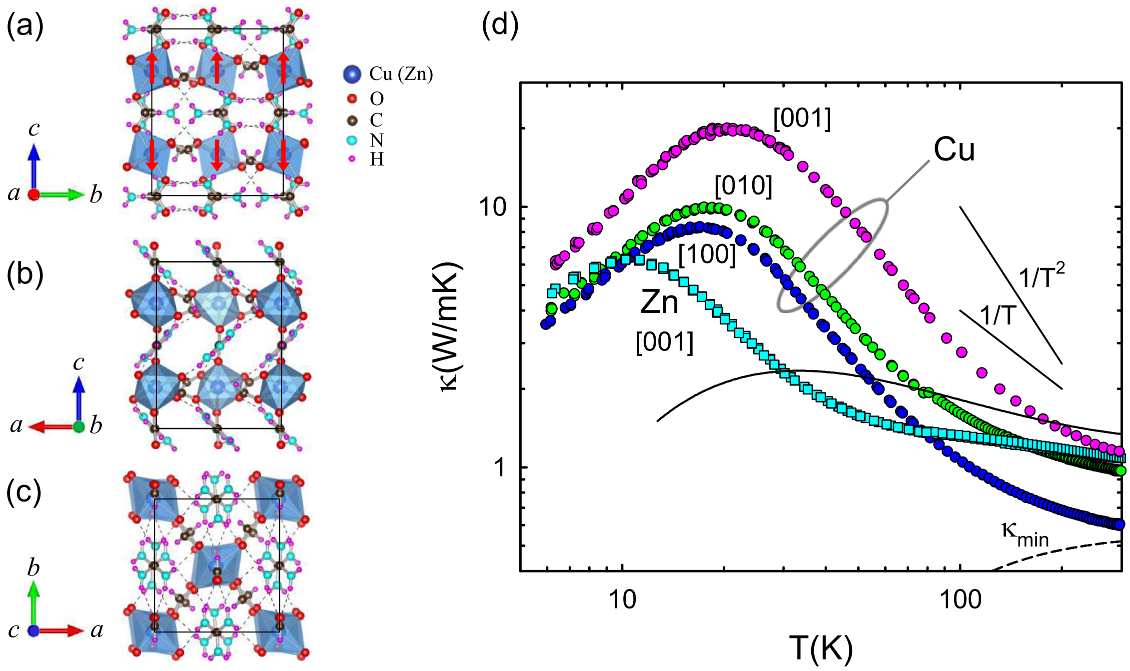

FIG. 1. (a)–(c) Crystal structure of the Cu and Zn MOFs (solid rectangles represent the unit cell and dashed lines represent the H bonds). Cu spins are depicted as red arrows in (a), showing their antiferromagnetic arrangement along the *c* axis (chains). Rendered with the VESTA software (Ref. 15). (d) Thermal conductivity of 1-Cu along principal crystallographic directions (circles) and of 2-Zn along the *c* axis (squares). Data for the [001] direction of single-crystalline [NH_2NH_3]Co($HCOO$)$_3$ from Ref. 12 are also shown (solid curve). The minimum thermal conductivity (see the text) is represented by the dashed curve.

guanidinium to the metal-oxygen octahedra. Anomalous phonon scattering in 2-Zn, revealed in the unusual behavior for its $\kappa(T)$, is attributed to the influence of this directionality on low-energy collective motions of the octahedra that have been implicated in its uniaxial negative thermal expansion.[19] The absence of this behavior in 1-Cu is attributed to the weakening of some N-H···O bonds due to the Jahn-Teller distortion of the CuO_6 octahedra. For heat flow along a direction preferentially transverse to the N-H···O bonds in 1-Cu, $\kappa \sim 0.6$ W/mK near 300 K, close to the theoretical minimum value. We also place an upper limit on a possible magnetic contribution to the heat transport along the quasi-one-dimensional AF chains of 1-Cu.

The syntheses of single crystals of 1-Cu and 2-Zn were carried out using reagent grade chemicals, without further purification, following the procedure described by Gao and coworkers.[3] 1-Cu was prepared via slow crystallization by slow evaporation over a week, and 2-Zn was prepared in an H-shaped glass tube over a two week time-period. The crystallographic structure and orientation of the crystals were determined by X-ray diffraction. Lattice parameters for the orthorhombic unit cell of the Cu compound ($Pna2_1$) were $a = 8.525(4)$ Å, $b = 9.033(2)$ Å, and $c = 11.356(3)$ Å, and for the Zn compound ($Pnna$),[20] $a = 8.347(4)$ Å, $b = 8.916(3)$ Å, and $c = 11.728(3)$ Å, in good agreement with those reported previously.[3] Crystals for 1-Cu were cut and polished into rectangular parallelepipeds with the longest dimension along the three principal crystallographic axes. The 2-Zn crystals grew as thin plates with the longest dimension along the *c* axis; data reported here are restricted to that direction as the *a*- and *b*-axis dimensions were too small for the measurement. The typical size for both 1-Cu and 2-Zn specimens was $1.2 \times 0.4 \times 0.2\,\text{mm}^3$ (the longest dimension along the heat flow). The thermal conductivity was measured in a diffusion-pumped probe using a standard steady-state method with the temperature gradient produced by a chip heater and monitored by a 25 μm diameter chromel-constantan differential thermocouple, both attached with stycast epoxy and dried at room temperature (to avoid complications for 1-Cu from partial decomposition which occurs[3] at temperatures above ∼100 °C). The combined heat losses via radiation and conduction through the leads were determined through separate experiments and the data corrected accordingly—these corrections, negligible at $T \leq 100$ K, amounted to ∼20%–30% at 300 K. The overall accuracy of the measurements is primarily determined by uncertainty in the separation of the thermocouple junctions, ∼20%. Two or more crystals were measured for each of the three transport directions, with good reproducibility in their magnitudes and temperature dependencies. Averaged data are presented here.

Figure 1(d) shows $\kappa(T)$ for heat flow along the three principal crystallographic directions for 1-Cu and along the [001] direction for 2-Zn. Notable features of the data are (1) the substantially lower temperature at which κ for 2-Zn rises to its maximum as compared to that of 1-Cu, (2) a substantial anisotropy of the thermal conductivity for 1-Cu, particularly the much lower value (by a factor of two) near 300 K along the *a* axis as compared to the other directions, and (3) the very low κ values near 300 K, approaching the theoretical minimum thermal conductivity[21–23] [dashed curve, Fig. 1(d)] discussed further below.

The general features of the $\kappa(T)$ data for 1-Cu are typical of crystalline insulators,[24] with a maximum at low temperatures (usually at a fraction of the Debye temperature, $T_{max} \sim \Theta_D/20$), and approximate $\propto 1/T$ decay at higher temperatures reflecting the increasing predominance of phonon-phonon scattering. With the kinetic theory expression as a guide, $\kappa \sim (1/3)Cv\ell$ (C is the lattice specific heat, v is the sound velocity, and ℓ is the phonon mean-free path), weaker T dependencies for $\kappa(T)$ at $T > T_{max}$ indicate additional scattering that limits the increase in ℓ with decreasing T. As observed in other single-crystalline HOIPs, the magnitude of the thermal conductivity near room temperature is quite low, $\kappa \lesssim 1$ W/mK. However, the order of magnitude increase in κ from room temperature to the maxima distinguishes the behavior of the present compounds from that of halide HOIPs[7–10] and the more closely related metal-organic framework compound,[12] $[NH_2NH_3]Co(HCOO)_3$ [solid curve, Fig. 1(d)]. The latter possesses a very similar framework to that of the present compounds but has $NH_2NH_3^+$ (hydrazinium) cations in place of guanidinium. A plausible explanation for the difference in their $\kappa(T)$ behaviors is a stronger and more isotropic NH⋯O bonding of the guanidinium cations to the framework in the present compound.[3,25–27] Presumably, the loose bonding of the NH_2 end of the hydrazinium and the overall asymmetry of hydrogen bonding to the oxygen of the transition-metal octahedra[25] allows for low-energy motions of molecular units which result in substantial scattering of heat-carrying acoustic-mode phonons to low temperatures in the hydrazinium compound.

The approximate $\kappa \propto T$ behavior evident at $T < T_{max}$, where $C \propto T^3$ is expected,[28] implies that ℓ continues to increase with decreasing T, with a predominance of phonon scattering having a frequency dependence,[29] $\ell(\omega) \propto 1/\omega^2$. Such low-$T$ behavior suggests scattering from extended defects[24] (e.g., stacking faults, precipitates, and other lattice distortions) and has been observed in measurements of κ for other metal-organic compounds.[30,31] The measurement of κ and specific heat to lower T would be of interest for further investigation.

Returning now to the data at $T > T_{max}$, note the much lower temperature upturn of κ along the [001] direction for 2-Zn which is unusual and unexpected. If there is a magnetic contribution to κ from spin excitations (κ_m) along the [001] direction of 1-Cu, to a first approximation, we expect it to add to the lattice contribution (κ_L), $\kappa = \kappa_L + \kappa_m$. No magnetic contribution transverse to the chains is to be expected given the quasi-one-dimensional nature of the antiferromagnetism.[3] Thus, a comparison of the 2-Zn κ data to that of 1-Cu along a and b clearly indicates that the scattering of heat-carrying phonons persists in 2-Zn to lower temperatures than in 1-Cu.

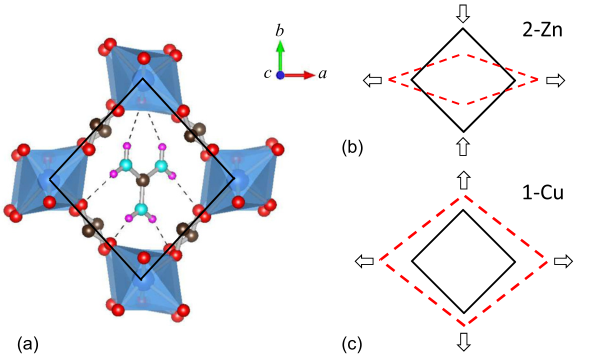

FIG. 2. (a) Framework structure of the octahedra in 1-Cu and 2-Zn (solid lines) and N-H⋯O bonds to guanidinium (dashed lines). H atoms of the formate molecules are omitted for clarity. Rendered with the VESTA software (Ref. 15). Also shown are models for the thermal expansion of (b) 2-Zn and (c) 1-Cu (adapted from Ref. 19). The dashed lines in (b) and (c) represent the frameworks at higher temperature.

Since the Cu and Zn masses hardly differ, this additional scattering must be attributed to the different character of Zn bonding within the anionic framework that alters the low-frequency vibrational spectrum of either the framework, the cations, or both. A recent study[19] of temperature-dependent thermal expansion (TE) in both 1-Cu and 2-Zn offers a clue to the surprising difference in the thermal conductivity of the two compounds: a negative TE is observed along the b-axis for 2-Zn, whereas 1-Cu has a positive TE for the same direction. This distinct behavior has its origin in the directionality of the six N-H⋯O bonds for both compounds [having substantially greater projection along the b axis, Fig. 2(a)] and the stretching and weakening of two of these bonds due to the Jahn-Teller distortion of CuO_6 octahedra in 1-Cu.

A "hinge-strut" model was introduced in Ref. 19 to explain the difference in the TE behavior. The expansion along a with increasing temperature is sufficiently large that it causes a contraction along b in 2-Zn [Fig. 2(b)] because of strong constraints on expansion imposed along b by the N-H⋯O bonds. A b-axis expansion is considerably less constrained in 1-Cu due to the weakened bonds, leading to a positive TE [Fig. 2(c)]. Such transverse bond motions of linker molecules that involve negligible deformation of polyhedral units (rigid-unit modes) have been shown to have a substantial weight in the low-energy vibrational spectra of MOFs and to play a critical role in negative TE.[32,33] Both translations and rotations of the octahedra in the present compounds with a relatively large amplitude and low frequency are expected, the sort of optic-mode phonons that can interact with and damp heat-carrying acoustic modes. Given that the least-constrained (floppiest) vibrations occur for atomic motions along the a axis for both compounds, the very different behavior of $\kappa_c(T)$ for 2-Zn motivates the hypothesis that a-axis-polarized transverse phonons propagating along the c axis of 2-Zn are more heavily damped than the corresponding phonons in 1-Cu due to their tighter coupling (through the NH⋯O bonds) to the polyhedra in adjacent ab-plane layers.

Turning to the anisotropy of κ in 1-Cu, the weaker transverse restoring forces associated with the N-H⋯O bonds along the a-axis likely suppress the dispersion for longitudinal acoustic phonons in this direction. In addition, the weaker, stretched H bonds associated with the Jahn-Teller effect should yield weaker restoring forces for b-axis-polarized transverse phonons propagating along a. The combination of these effects is the likely cause of a much lower κ_a in 1-Cu, where $\kappa_b \sim \kappa_c \sim 1$ W/mK near 300 K and $\kappa_a \sim 0.6$ W/mK. The latter is comparable to the theoretical minimum conductivity[21–23] [dashed curve, Fig. 1(d)], computed[34] using longitudinal (v_l) and transverse (v_t) sound velocities estimated from expressions suitable for isotropic solids[35]

$$v_l = \left[\frac{Y}{\rho}\frac{1-\nu}{(1-2\nu)(1+\nu)}\right]^{1/2}$$

$$v_t = \left[\frac{Y}{2\rho(1+\nu)}\right]^{1/2}, \tag{1}$$

where Y is the Young's modulus, ρ is the mass density, and ν is Poisson's ratio. We took $Y = 17.5$ GPa from measurements[36] for 1-Cu,

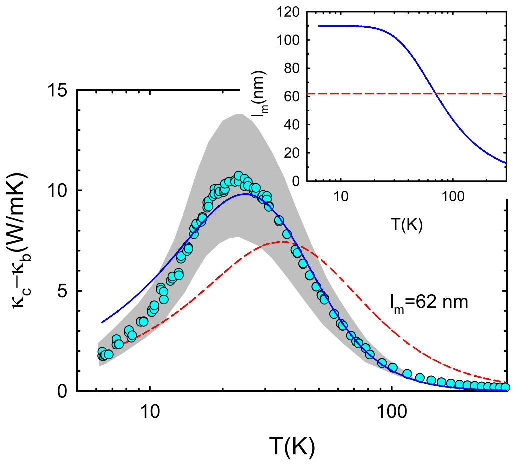

FIG. 3. Difference, $\kappa_c - \kappa_b$, for $[C(NH_2)_3]Cu(HCOO)_3$. The shaded region reflects the uncertainty in the difference of the two measured κ curves (28%). The solid and dashed curves are computed from Eq. (2) for a spinon mean-free path given, respectively, by a constant $l_m = 62$ nm and $l_m = [l_0^{-1} + AT\exp(-T^*/T)]^{-1}$ with $l_0 = 110$ nm, $T^* = 77$ K, and $A = 3\times10^5$ m^{-1} K^{-1}. The inset shows the corresponding $l_m(T)$ curves.

$\rho = 2$ kg/m^3, and $\nu = 0.3$ (typical for a variety of solids[37]), to find $v_l = 3.43$ km/s and $v_t = 1.84$ km/s.

Finally, we comment on a possible magnetic contribution to κ along the quasi-one-dimensional AF chains (c axis) of 1-Cu that might account for $\kappa_c > \kappa_b$ throughout most of the temperature range. Although we had anticipated the prospect of using κ_c for 2-Zn as a nonmagnetic reference for the lattice contribution to κ_c in 1-Cu, the anomalous lattice conduction unique to 2-Zn makes this unreliable. In the absence of a suitable reference material, it is typical in the study of low-dimensional magnetic compounds to estimate the magnetic contribution by assuming the isotropy of the lattice contribution. Clearly, this assumption would be uncertain for 1-Cu, given the anisotropy in the lattice heat conduction implied by the observed difference in κ along the a and b axes (transverse to the chains). Nevertheless, it is informative to determine an *upper bound* estimate of κ_m from the difference, $\kappa_c - \kappa_b$ (Fig. 3), and compare its magnitude and temperature dependence to theoretical models.

The fundamental quasiparticle excitations of quasi-1D AF chains are spinons with a thermal conductivity for a gapless $S = 1/2$ Heisenberg chain given by[13]

$$\kappa_m = \frac{2n_s k_B^2}{\pi\hbar} T \int_0^{\pi J/2k_BT} \frac{x^2 e^x}{(e^x-1)^2} l(x,T)\,dx, \tag{2}$$

where $n_s = 2/(ab)$ is the number of spin chains per unit area [Fig. 1(c)] transverse to the chains, $x = \epsilon/k_BT$ is the normalized energy, $J/k_B = 68$ K is the nearest-neighbor AF exchange energy as determined from the modeling of the magnetic susceptibility,[3] and $l_m(x,T)$ is the spinon mean-free path that can depend on both the energy and temperature. We considered a constant mean-free path model, $l_m = l_0$, and another for which thermally activated spinon–phonon scattering is incorporated,[38,39] $l_m = [l_0^{-1} + AT\exp(-T^*/T)]^{-1}$ (dashed and solid curves, respectively, Fig. 3). Theory describes the magnitude and temperature dependence reasonably well, with l_m at low-T $\sim 100-200$ times the distance between neighboring spins, an order of magnitude smaller than that found for the cleanest quasi-one-dimensional antiferromagnets.[39]

In summary, the preferential orientation of N-H⋯O bonds along the b axis of 1-Cu and 2-Zn and a Jahn-Teller-induced weakening of these bonds in 1-Cu are implicated in surprisingly different $\kappa(T)$ behaviors for the two compounds and substantial anisotropy of κ in 1-Cu. Anomalous $\kappa(T)$ along the c axis of 1-Zn implicates a mechanism of enhanced damping for a-axis-polarized transverse acoustic phonons involving collective motions of rigid octahedra which is consistent with observations of negative thermal expansion observed along the b axis.[19] An extremely low value of κ along the a-axis for 1-Cu at 300 K approaches the theoretical minimum value for crystalline materials. A magnetic contribution to κ along the quasi-1D AF chains of the Cu compound is not definitively established given the lattice anisotropy, but the analysis of an upper-bound estimate of this contribution implies spinon scattering parameters consistent with those found for other AF chain compounds. These observations highlight the sensitivity of heat conduction to probe the directionality and flexibility of H-bonded molecular linkers in MOF compounds and their influence on low-energy vibrational properties.

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