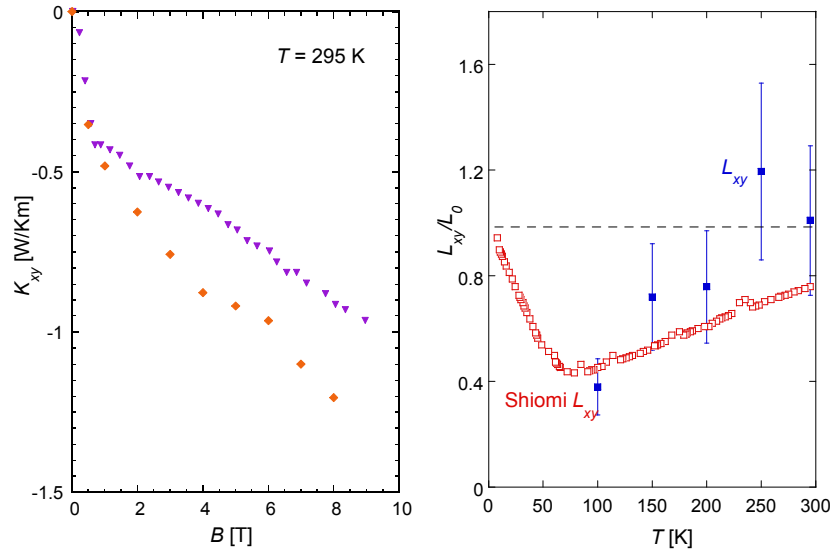


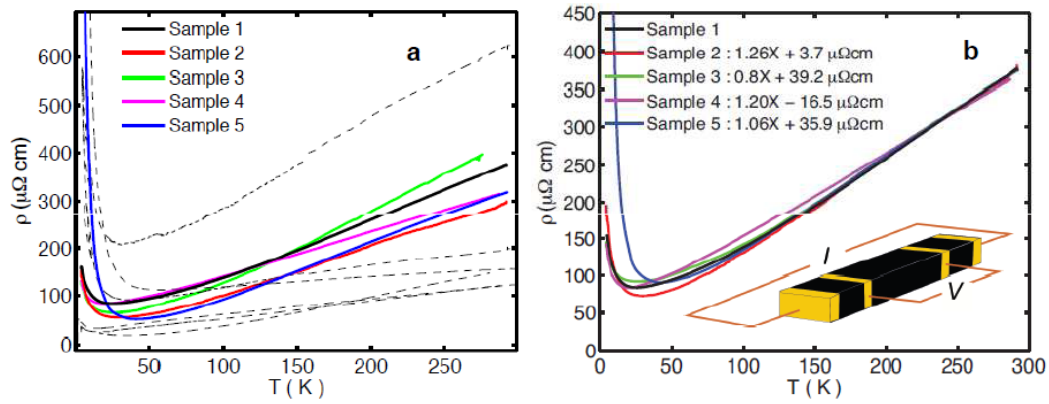
Supplementary Information

Gross violation of the Wiedemann-Franz law in a quasi-one-dimensional conductor

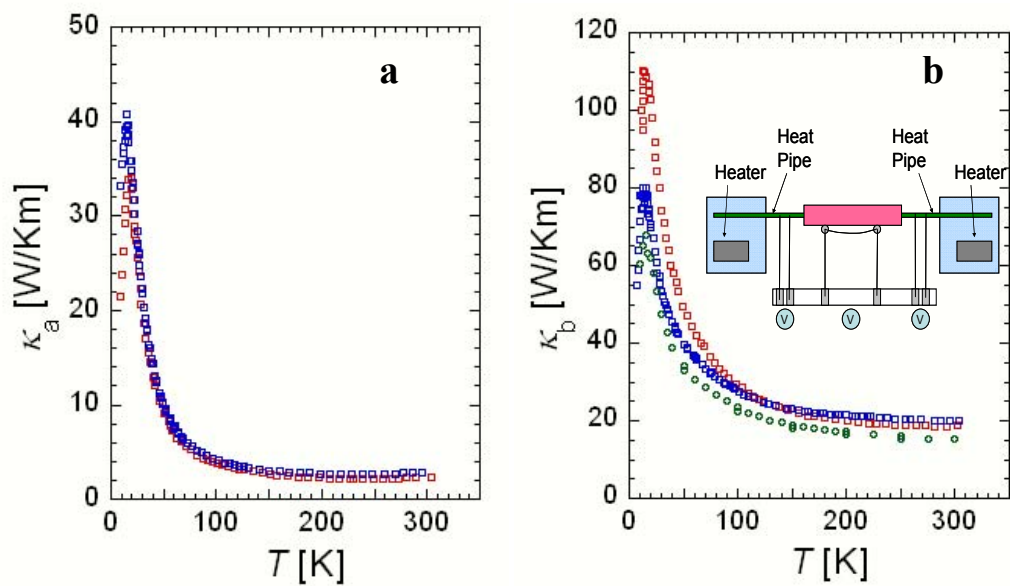
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Supplementary Figure S1. Lorenz ratio in nickel. **a.** Thermal Hall conductivity in Ni at $T = 295$ K as measured in our experimental set-up (closed diamonds) and by Shiomi *et al.* [38] (inverted triangles). **b.** Hall Lorenz number of Ni. Measured data is shown as closed blue squares, with data from [38] shown as open red squares. It should be noted that the Hall Lorenz ratio was calculated from data above 2 Tesla, i.e. away from the anomalous region.



Supplementary Figure S2: Temperature dependence of the b -axis (intra-chain) resistivity of $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$. **a.** Resistivity measurements taken on 11 different samples with current predominantly along the b -axis but with varying degrees of mixing of the resistivity tensor components. A subset of 5 curves was determined to be closest to pure b -axis resistivity, shown with solid lines. **b.** Scaling of the temperature dependence of the resistivity for the subset of the curves taken from Supplementary Figure S2a. The inset shows the sample mounting configuration.



Supplementary Figure S3. Thermal conductivity of $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$. Thermal conductivity measurements of multiple $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ single crystals along the crystallographic a -axis (a) and b -axis (b). Inset shows schematic diagram of the experimental setup.

Supplementary Methods

Verification of the Wiedemann-Franz Law in Nickel

The accuracy of our experimental set-up was tested by measuring the Hall Lorenz number L_{xy} in 99.9% pure nickel foil. The closed diamonds in Supplementary Figure S1a represent κ_{xy} measured as a function of applied field ($\mathbf{H}/c$) at $T = 295$ K. For comparison, the inverted triangles are corresponding data taken on a single crystal of Ni by Shiomi *et al.* [38]. Although the quality of the samples is different (as evidenced by their different resistivity curves), the overall shape and magnitude of $\kappa_{xy}(H)$ are very similar, including the kink at low field that corresponds to the saturation of the anomalous Hall component.

Supplementary Figure S1b shows L_{xy} measured at 50 K intervals between 100 K and 300 K. As expected, L_{xy}/L_0 is approximately equal to unity at 300 K, then as T decreases, L_{xy}/L_0 falls to about half its room temperature value. Also shown in Supplementary Figure S1b is data from the more detailed study by Shiomi *et al.* [38]. Within our experimental uncertainty, our data are qualitatively and quantitatively consistent with theirs. This level of consistency confirms that the values of L_{xy} exceeding $L_0 \times 10^4$ obtained on $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ are not an artefact of our experimental set-up.

Isolating the intrinsic in-chain resistivity in $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$.

In order to test the validity of the Wiedemann-Franz (WF) law, accurate measurements of both the electrical resistivity and thermal conductivity are essential. In order to isolate the in-chain (diagonal) component of the electrical conductivity tensor, extreme care is needed to electrically short out the sample in the two directions perpendicular to the chain and thus ensure that current flow between the voltage contacts is uniaxial. In our experiments, this is achieved either by coating conductive paint or evaporating gold strips across the entire width of the sample in the two orthogonal current directions. The mounting configuration is shown as an inset in Supplementary Figure S2b.

In total, we measured $\rho_b(T)$ of over 30 single crystals to allow us to better identify the

intrinsic T -dependence of the chains. A sub-set of these measurements is shown in Supplementary Figure S2a. The curves in faint dashed lines feature small contributions from the other components of the resistivity tensor, which can be either positive or negative. Only a restricted subset of these curves, plotted as solid lines in Supplementary Figure S2a, display the same temperature dependence within a scaling factor and a constant offset. Note that traces featuring negative resistivity values or resistivity values larger than 1 m Ω cm were discarded and are not shown.

In order to highlight the reproducibility of the resistivity behaviour of samples 1-5, we re-plot in Supplementary Figure S2b the same subset of curves, normalized using scaling factors and constant offsets of at most 26% of the corresponding room temperature value. This uncertainty reflects predominantly our uncertainty in our estimate of the distance between voltage contacts, though the offsets may also signify small additional contributions from one or both of the interchain current paths. Note that none of the other traces plotted in Supplementary Figure S1a could be overlaid as in Supplementary Figure S2b for any choice of scaling factor and/or offset. For the purposes of calculating the longitudinal and Hall Lorenz ratios in the manuscript, we have assumed that $\rho_b(T)$ of sample 1 represents the intrinsic b -axis component of the resistivity tensor. The corresponding resistivity anisotropy (i.e. $\rho_a:\rho_b:\rho_c$) also agrees quantitatively with the measured anisotropy of the optical conductivity (24) as well as the upper critical field in superconducting Li_{0.9}Mo₆O₁₇ [J-F. Mercure *et al.*, to be published]. Note that even with these significantly lower estimates of $\rho_b(T)$, the WF law is still strongly violated in Li_{0.9}Mo₆O₁₇.

Reproducibility in the thermal conductivity measurements

In highly anisotropic materials, heat and charge flow can take very different routes to the contacts. In a system with anisotropic thermopower, this can lead to electrical currents flowing in the steady state (where usually there are none), which in turn can lead to additional heating/cooling effects, such as Thomson heating or the Peltier effect. The only way that all components of the current density can vanish in the steady state (at least in zero-field) is by ensuring that the thermal gradient in the sample is uniaxial. These effects are described in detail in a recent theoretical treatment by Silk and Schofield [39].

The anisotropy in the thermal response in $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ is one order of magnitude lower than in the electrical resistivity (due primarily to the phonon contribution), making the conditions for uniaxial heat flow significantly less stringent than for the electrical resistivity. Nevertheless, a similar degree of care is taken to isolate the individual components of the thermal conductivity tensor, in particular the heat pipes are always connected to the sample in such a way that any heat flow orthogonal to the (long) sample axis is minimised. Again, the reproducibility of our data for different samples, as illustrated in Supplementary Figure S3, gives us confidence that we are indeed measuring the intrinsic *a*- or *b*-axis longitudinal thermal conductivity.

Possible internal heating effects in thermal Hall measurements

Given the fact that in a thermal Hall effect measurement there are two thermal gradients generated in the sample, any anisotropy in the thermopower can lead to the development of thermoelectric eddy currents [39,40]. These in turn give rise to the possibility of three additional internal heating (or cooling) effects; the Peltier effect (arising from intrinsic inhomogeneity of the samples), the Thomson effect (due to variations in thermopower throughout the sample) and the Bridgman effect (due to changes in the direction of the current) [39]. The influence of these various source terms on the measured thermal Hall conductivity, and whether they lead to an enhanced or reduced transverse thermal gradient, is very difficult to ascertain however. Nevertheless, as discussed below, inspection of the sources of each of these different heating effects makes it seem unlikely that any of them are responsible for the large value of the Hall Lorenz number, and the corresponding violation of the Wiedemann-Franz law, found in $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$.

Firstly, given the crystalline quality of our $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ crystals (determined using a single crystal diffractometer) and the fact that samples cleaved from the same piece of single crystal show highly reproducible transport behaviour, it would appear that our $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ crystals possess a high degree of homogeneity. This would appear to rule out any significant Peltier effect in our thermal Hall measurements. Secondly, since thermoelectric eddy currents are circulatory in nature, we expect that any heating or cooling effects generated by the Bridgman effect would be effectively cancelled out. In this respect, it is worth noting that the values of ΔT_y do not depend on the precise

location of the differential thermocouple on the sample. Finally, both the b -axis thermopower [41] and the ab -plane Nernst coefficient of $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ [Wakeham *et al.* to be published] go through a maximum as a function of temperature, at a temperature between 50 K and 100 K. In this region, the Thomson effect, which is proportional to the temperature derivative of either the diagonal or off-diagonal component of the thermopower (depending on the geometry of the experimental set-up), must vanish. By contrast, our thermal Hall data show a monotonically increasing κ_{xy} and corresponding L_{xy} across the same temperature range, implying that the Thomson effect itself cannot be a dominant factor in our measurements.

In order to measure the thermal Hall effect, the same set-up on which the longitudinal (zero-field) thermal conductivity measurements were performed was used, although in this case, the differential thermocouple was positioned on opposite edges of the crystal. The sample was always positioned so that the heat flow in the longitudinal direction was along the b -axis of the sample. The experiment was placed in an evacuated chamber immersed in liquid helium within the coil of a superconducting magnet. Heating power was provided by a resistive element thermally connected to the experimental platform and was controlled by a Lakeshore temperature controller. During a measurement of the thermal Hall effect the temperature was first stabilised, then a fixed field applied and finally heat current passed through the sample. The modified steady state method was then employed as before. The power loss was found to be $\sim 20\%$ at room temperature, reducing to $\sim 10\%$ below 200K. The experiment is then repeated at multiple field values. In order to isolate the thermal Hall response, both positive and negative polarities of the magnetic field were used. As with the longitudinal thermal conductivity measurements, the heat direction was then reversed and the measurements repeated.

Supplementary References

38. Shiomi, Y. *et al.* Effect of scattering on intrinsic anomalous Hall effect investigated by Lorenz ratio. *Phys. Rev. B* **81**, 054414 (2010).
39. Silk, T. W. Silk & Schofield, Thermoelectric effects in anisotropic systems: measurement and applications. /condmat0808.3526v1.
40. Samoilovich, A. G. & Korenblit, L. L. Thermoelectric eddy currents in an anisotropic material. *Sov. Phys. – Solid State* **3**, 1494 (1962).
41. Boujida, M. *et al.* Superconducting properties of the low dimensional lithium molybdenum purple bronze *Physica C* **153-155**, 465 (1988).