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Anomalously low electronic thermal conductivity in metallic vanadium dioxide

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In electrically conductive solids, the Wiedemann-Franz law requires the electronic contribution to thermal conductivity to be proportional to electrical conductivity. Violations of the Wiedemann-Franz law are typically an indication of unconventional quasiparticle dynamics, such as inelastic scattering, or hydrodynamic collective motion of charge carriers, typically pronounced only at cryogenic temperatures. We report an order-of-magnitude breakdown of the Wiedemann-Franz law at high temperatures ranging from 240 to 340 kelvin in metallic vanadium dioxide in the vicinity of its metal-insulator transition. Different from previously established mechanisms, the unusually low electronic thermal conductivity is a signature of the absence of quasiparticles in a strongly correlated electron fluid where heat and charge diffuse independently.

In a Fermi liquid, the same quasiparticles that transport charge also carry heat. Therefore, in most normal metals the charge and heat conductivities are related via the Wiedemann-Franz (WF) law: The ratio between the electronic thermal conductivity ($\kappa_e$) and the product of electrical conductivity ($\sigma$) and absolute temperature ($T$) is a constant called the Lorenz number, $L = \kappa_e/\sigma T$, typically not very different from the Sommerfeld value $L_0 = (\pi^2/3)(k_B/e)^2 = 2.44 \times 10^{-8}$ W ohm$^{-1}$ K$^{-2}$ (where $k_B$ is the Boltzmann constant and $e$ is the electron charge). Recently, violations of the WF law have been theoretically predicted (1–4) or experimentally observed (5–13) in some electronic systems. However, with one exception observed in a one-dimensional conductor at room temperature (13), these violations typically occur at cryogenic temperatures and arise from unconventional phases of matter, strong inelastic scattering of quasiparticles, or semimetal physics. Here we report a drastic breakdown of the WF law at high temperatures, with $L$ smaller than $L_0$ by an order of magnitude, in a strongly correlated metal (vanadium dioxide (VO$_2$)). The observed anomalously low electronic thermal conductivity is accompanied by an unusually high electronic thermoelectric figure of merit; tungsten is determined by $L_0$ (where $k_B$ is the Boltzmann constant). The WF law is attributed to the formation of a strongly correlated, incoherent non-Fermi liquid, in which charge and heat are independently transported by distinct diffusive modes at high temperatures rather than carried by long-lived quasiparticles (14, 15).

We observed the effect in the metallic phase of VO$_2$ in the vicinity of its metal-insulator transition (MIT). VO$_2$ undergoes the MIT at 340 K, accompanied by a first-order structural phase transition from the monoclinic insulating (I) phase to the tetragonal metallic (M) phase on heating (16). In this work, $\kappa_e$ is determined by subtracting the phonon (lattice) thermal conductivity ($\kappa_{\text{ph}}$), obtained by combining first-principles calculations with x-ray scattering measurements, from the measured total thermal conductivity ($\kappa_{\text{tot}}$). Previously, $\kappa_{\text{tot}}$ of VO$_2$ has been measured in bulk and thin films with conflicting conclusions. In bulk VO$_2$, for example, it was reported that $\kappa_{\text{tot}}$ stays constant (17) or decreases very slightly (18) with increasing $T$ across the MIT. Unknown electronic scattering leading to a possible failure of the WF law in VO$_2$ was alluded to nearly half a century ago (17), but this has not been experimentally or analytically investigated. Recently, however, time-domain thermal reflectance measurements on polycrystalline VO$_2$ films showed an increase in $\kappa_{\text{tot}}$ with a magnitude seemingly consistent with the WF law (19). Unlike in those measurements, we use single-crystal VO$_2$ nanobeam, where the single crystallinity and freestanding configuration in our measurements eliminate extrinsic domain and strain effects. Moreover, our sample geometry ensures that both heat and charge flow in the same path along the nanobeam length direction. This is a crucial condition that, if not satisfied, could result in an erroneous determination of $\kappa_e$ and assessment of the WF law, especially for VO$_2$, which has an anisotropic crystal structure. The single-crystal VO$_2$ nanobeam were grown by the previously reported vapor-transport method (20–22) (see materials and methods, along with figs. S1 and S2). Figure 1A shows a nanobeam bonded to two microfabricated, suspended pads for simultaneous measurements of $\kappa_{\text{tot}}$, $\sigma$, and the Seebeck coefficient (23, 24) (details in materials and methods, as well as figs. S3 and S4). The thermal and electrical contact resistances were determined to be negligible (materials and methods; see also figs. S5 and S6).

The measured $\kappa_{\text{tot}}$ of a representative VO$_2$ nanobeam is shown in Fig. 1B. Consistent with a previous study on bulk VO$_2$ (17), our nanobeam exhibit very little change in $\kappa_{\text{tot}}$ across the MIT: $\Delta\kappa_{\text{tot}}^\text{bulk} \approx 0.2$ W/m K. More than five VO$_2$ nanobeam with different sizes were measured, and all show $\Delta\kappa_{\text{tot}}^\text{bulk}$ at this level or lower (materials and methods and fig. S8). From the measured $\sigma$ of the nanobeam across the MIT, the expected electronic thermal conductivity ($\kappa_e^\text{bulk}$) for conventional Fermi liquid transport can be calculated, assuming that both phases obey the WF law ($L = L_0$). With $\sigma$ rising from 4.6 × 10^3 S/m (I phase) to 8.0 × 10^5 S/m (M phase) (where $L_0 = 1.6 A/V$), $\kappa_e^\text{bulk}$ exhibits an abrupt jump from nearly zero to 69 W/m K (Fig. 1B). The measured $\Delta\kappa_{\text{tot}}^\text{bulk}$ is less than 3% of $\kappa_e^\text{bulk}$ in the M phase. Considering that $\kappa_e^\text{bulk}$ alone in the M phase is already greater than the measured $\kappa_e$, application of the WF law would imply an unphysical, negative $\kappa_e$ in the M phase.

To better understand this anomaly, we determined $\kappa_{\text{ph}}$ in both I and M phases ($\kappa_{\text{ph}}^\text{I}$ and $\kappa_{\text{ph}}^\text{M}$) by combining first-principles calculations with measurements (details in materials and methods and fig. S9). As a first step, the phonon dispersions were calculated using density functional theory (DFT), as shown in Fig. 2A for both I and M phases. From these dispersions, both the phonon group velocity and lattice specific heat were obtained for different phonon modes and wave vectors. Next, on the basis of anharmonic (umklapp) phonon scattering in a pure bulk sample, a full first-principles calculation (25) was performed for the phonon relaxation time in the I phase. In this phase, a calculated bulk value of $\kappa_{\text{ph}}^\text{bulk}$ = 6.46 W/m K was obtained at $T = 340$ K along the rutile-phase $c$ axis (the nanobeam length direction). To evaluate the final nanobeam phonon thermal conductivity ($\kappa_{\text{ph}}^\text{MB}$), Matthiessen’s rule was then applied to account for...
impurity and diffuse boundary scattering of phonons. Using the known rectangular cross section, this boundary scattering (26) reduces $\kappa_{el}^0$ from 6.46 W/m·K for the bulk to 6.15 W/m·K for the nanobeam, very close to the experimentally measured value of 5.8 W/m·K (Fig. 1B). The remaining small difference is attributed to scattering from impurities, most probably atomic vacancies as native point defects (supplementary materials).

For the M phase, evaluating the thermal conductivity solely using first-principles calculations is challenging because VO$_2$ is a strongly correlated electron system that could exhibit both strong electron-electron and electron-phonon interactions (25). In addition, phonon scattering has not been successfully calculated with current theoretical techniques. However, previous ab initio molecular dynamics simulations within the framework of DFT were successful in predicting anharmonically renormalized phonon dispersions in the M phase, which were in good agreement with energy- and momentum-resolved inelastic x-ray scattering (IXS) experiments previously reported in (25). Using these M-phase first-principles phonon dispersions (Fig. 2A) benchmarked against experiments, together with the phonon scattering rates obtained from the IXS measurements (details in materials and methods and fig. S9), we determined $\kappa_{ph}^{M,\text{bulk}} = 5.72$ W/m·K (Fig. 2B), a reduction by 13% from $\kappa_{ph}^{I,\text{bulk}}$. Note that this value includes umklapp, electron-phonon scattering, and all other possible scattering of phonons in bulk, defect-free VO$_2$. With this value of $\kappa_{ph}^{M,\text{bulk}}$ using the Matthiessen’s rule similar to that used in the I phase, the nanobeam $\kappa_{ph}^{M,\text{I}}$ for the M phase was obtained. With both boundary and impurity scatterings considered, $\kappa_{ph}^M$ and $\kappa_{ph}^I$ for nanobeams become even closer to each other (Fig. 2B). The electronic thermal conductivity in the M phase ($\kappa_{el}^M$) can then be obtained by subtracting the nanobeam value of $\kappa_{el}^I$ from the measured $\kappa_{el}^M$. In this way, we obtained $\kappa_{el}^M = 0.72$ W/m·K and, hence, an effective Lorenz number $L_{\text{eff}} = (k_e^2/k_p^2)\cdot L_0 = 0.11L_0$, corresponding to a suppression of $L$ by nearly an order of magnitude. Although the uncertainty of $k_e^2$ is high compared with $k_e^2$ itself (~80%), $L_{\text{eff}}/L_0$ is still low, with an upper bound of less than 0.2.

We now show that this effect can be tuned in W-doped VO$_2$ (W$_x$V$_{1-x}$O$_2$) nanobeams. Tungsten was chosen as the dopant because it is known to lower the MIT temperature ($T_{\text{MIT}}$) by detwisting the V-V bonds in the monoclinic I phase (16). The effects of W doping on thermal and electrical transport over a wide T range are summarized in Fig. 3, A and B. As can be seen from the electrical conductivity curves, $T_{\text{MIT}}$ decreases monotonically with the W-doping fraction $x$ at a rate of ~21 K per atomic % (fig. S1), consistent with previous reports (21, 27). The W$_x$V$_{1-x}$O$_2$ nanobeams show a clear jump in $\kappa_{el}$ across their MIT, accompanying the abrupt jump in $\sigma$, in marked contrast to the behavior of undoped VO$_2$. To determine $L_{\text{eff}}$ in the M phase of W$_x$V$_{1-x}$O$_2$, we obtained $\kappa_{el}^{M}$ in a similar way as for the undoped VO$_2$ nanobeams by considering both boundary scattering and the (now substantial) impurity scattering in the I and M phases of W$_x$V$_{1-x}$O$_2$.

It can be seen from Fig. 3C that $L_{\text{eff}}$ increases toward $L_0$ as a function of $x$ (summarized in table S2). In the W$_x$V$_{1-x}$O$_2$ samples, the average W-W distance is estimated to be ~1 nm, larger than our estimated quasiparticle mean free path of electrons in the M phase (~0.5 nm) (materials and methods section S10). With these levels of W doping, the added elastic scattering from the dopants may partially contribute to the rise in $L_{\text{eff}}$ for W$_x$V$_{1-x}$O$_2$. To elucidate the mechanism behind the vast suppression in $L_{\text{eff}}$ and its partial recovery to the normal value with W doping, the Seebeck coefficient ($S$) of these nanobeams was also measured. The measured $S$ can be used...
to distinguish different scenarios that all lead to a very small $L_{\text{eff}}$. The dimensionless electronic figure of merit, $S^2/L = S^2T/(\kappa_c T)$, is $\sim 10^{-4}$ for a conventional metal such as copper. Our measurements (Fig. 3C) instead show that $S^2/L = 0.11$ for the M phase of VO$_2$ (summarized in table S2). Such a large value of $S^2/L$ for a metal is indicative of nonquasiparticle physics, because the factor $\kappa_c T$ (where $\kappa_c$ is the Fermi energy) that usually suppresses transport and charge must proceed through collective and independent diffusion (14). Hence, the Lorenz ratio of their conductivities has no reason to take the value $L_0$. Instead, the Lorenz ratio is proportional to the electronic specific heat over charge compressibility. For such systems in the high temperature limit (above the renormalized bandwidth), the temperature dependence of these thermodynamic quantities is relatively insensitive to interactions. Estimates then show that, in general, $L_{\text{eff}}$ becomes very small, as the specific heat vanishes more rapidly than the charge compressibility with temperature (14) (see supplementary materials). Although $L_{\text{eff}}$ numerically recovers toward $L_0$ with W doping, the linear temperature dependencies of the resistivity (Fig. 3B) and $S$ (Fig. 3D) in the M phase are qualitatively unaltered. The collapse of $S$ with different W doping levels onto the same temperature dependence, as well as the increase of resistivity with doping in the M phase, indicates that the material remains a “bad metal” with W doping, suggesting the continued absence of long-lived quasiparticles. As $T_{\text{MIT}}$ is lowered with doping, temperatures close to $T_{\text{MIT}}$ (where $L_{\text{eff}}$ is measured) are moving away from the asymptotic high-$T$ regime. Therefore, at lower temperatures, although charge and heat diffusions remain independent, one no longer expects $L_{\text{eff}} \ll L_0$ instead, $L_{\text{eff}}$ is expected to increase (14). A strong electron-phonon interaction may potentially couple $\kappa_c$, resulting in incomplete separability of $\kappa_c$ and $\kappa_s$ in the M phase. However, the electron contribution to the observed $\kappa_{\text{eff}}$ would still remain anomalously low. This allows VO$_2$ a model system to probe unusual charge behavior in “bad metals.” As the decoupled, collective transport of charge and heat occurs universally in incoherent electron fluids, these effects are expected to exist generally in a wide variety of strongly correlated electronic materials and can be explored with our experimental methodology. The Lorenz number thus provides a window into the unconventional electronic dynamics of these materials.

Fig. 3. Breakdown of the WF law from thermal and electrical conductivities of VO$_2$ and W$_x$V$_{1-x}$O$_2$ nanobeams. (A) Experimentally measured $\kappa_{\text{tot}}$ of W$_x$V$_{1-x}$O$_2$ nanobeams. (B) Four-probe electrical conductivity $\sigma$ versus $T$ for the same set of W$_x$V$_{1-x}$O$_2$ nanobeams. $T_{\text{MIT}}$ shifts toward lower $T$ with W doping. (C) Extracted, normalized Lorenz number as a function of $x$. $L_{\text{eff}}$ is obtained from $(\Delta \kappa_0 - \Delta \kappa_{\text{tot}})/(\sigma T)$, and the red solid line is a guide for the eye. Also shown is the $M$-phase $S^2/L_{\text{eff}}$ with $x = 0, 2.1, 4.5$% at $T_{\text{MIT}}$ of 341, 312, and 240 K, respectively. The blue solid line is a guide for the eye. $S^2/L_{\text{eff}}$ for a conventional metallic conductor, copper, is also shown for comparison (blue dashed line). Error bars mostly stem from uncertainties of total thermal conductivities and phonon linewidths. (D) Measured Seebeck coefficient $S$ versus $T$ for the M phase of the VO$_2$ and W$_x$V$_{1-x}$O$_2$ nanobeam. (Inset) $S$ over a wider temperature range covering both the I and M phases. In all panels, filled (or open) symbols connected with solid (or dotted) lines represent the data collected during heating (or cooling).

REFERENCES AND NOTES


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SUPPLEMENTARY MATERIALS
www.sciencemag.org/content/355/6323/371/suppl/DC1
Materials and Methods
Figs. S1 to S11
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References (34–74)
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Editor's Summary

Decoupling charge and heat transport
In metals, electrons carry both charge and heat. As a consequence, electrical conductivity and the electronic contribution to the thermal conductivity are typically proportional to each other. Lee et al. found a large violation of this so-called Wiedemann-Franz law near the insulator-metal transition in VO$_2$ nanobeams. In the metallic phase, the electronic contribution to thermal conductivity was much smaller than what would be expected from the Wiedemann-Franz law. The results can be explained in terms of independent propagation of charge and heat in a strongly correlated system.

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