its regime of validity to fortify claims that 30 K would be the upper limit for electron–phonon coupling."

The above comment may not be entirely fair if its subject is the analysis McMillan made in a 1968 article,[1] in which he doesn't mention 30 K as a possible maximum value of T_c but does list 9.2, 22, 28, and 40 K as possible maximums. None of those temperatures are the upper limit of electron–phonon coupling in general. Rather, they are upper limits of T_c in classes of materials represented by lead, niobium, and niobium–tin and vanadium–silicon alloys, and they have not exceeded the regime of validity of the McMillan equation. In particular, McMillan does not exclude higher T_c in other classes, provided that λ does not exceed 2 in his equation.

Specifically, McMillan realizes that T_c from his equation declines when, on average, the phonon frequency becomes either too large or too small and searching for maximum T_c leads to $\lambda = 2$. Since in 1968 it was believed that $T_c = 7.2$ K and $\lambda = 1.3$ in Pb, McMillan concludes that T_c may reach 9.2 K in a Pb alloy when $\lambda = 2.8$. In that case, T_c was found numerically and therefore was not subject to the $\lambda < 2$ limit. Had, say, McMillan found $T_c = 203$ K with $\lambda = 1.3$ from a material in his day, he likely would have concluded that T_c could be higher still in a similar material with $\lambda = 2.8$.

In recent work,[2] we extended the McMillan equation for $0.6 < \lambda < 2.67$. We found that the original McMillan equation is indeed highly accurate if $\lambda < 2$. We also predicted that T_c can reach ~44 K in a beryllium–lead alloy, when the Be to Pb ratio is 0.58 to 0.42 ($\lambda = 1$ and Debye temperature is 871 K). Our result may be useful to experimenters because it not only shows that T_c may be high in a class of alloys, but it also gives the exact composition of the alloy, hopefully without extreme pressure.

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The article by Warren Pickett and Mikhail Eremets on room-temperature superconductivity in hydrides had me thinking about the role of specific heat in superconductivity research.

Heike Kamerlingh Onnes and Gilles Holst reported in 1914 that "with respect to the specific heat, nothing peculiar happens" at mercury's superconducting transition,[1] which Kamerlingh Onnes had discovered three years earlier. Twenty years later, after technical advances in cryogenics and thermometry, Kamerlingh Onnes's former student, Willem Keesom, and J. A. Kok discovered a specific heat jump at the critical temperature T_c, without latent heat.[1] It was misinterpreted as a sudden drop in Debye temperature, which assumes phonons are the predominant contributor to specific heat, even though the free electronic model for electronic specific heat ($C_e = \gamma T$) had been proposed before then. It took almost another 20 years for the superconducting-state electronic specific heat (C_{es}) to be identified, but still erroneously concluded as having a T^3 dependence. Eventually, experimental data covering a wider (T_c/T) range confirmed the exponential-temperature dependence of its electronic origin.[2]

In their 1957 article, John Bardeen, Leon Cooper, and J. Robert Schrieffer opened with the statement, "The main facts which a theory of superconductivity must explain are (1) a second-order phase transition at the critical temperature, T_c, (2) an electronic specific heat varying as $\exp(-T_0/T)$ near $T = 0$ K and other evidence for an energy gap."[3] The rest is now history.

In my opinion, superconducting hydrides may provide opportunities for studying C_{es} in detail over an exceptionally broad (T_c/T) range. Intuitively, the near-room-temperature transition would make it impossible to delineate the electronic and the lattice contributions from total specific heat ($C = C_e + C_\ell$) being obtained calorimetrically. That appears to be a valid concern for cuprate superconductors with T_c near or above 90 K. In contrast, for metallic hydrogen with an exceedingly high Debye temperature[4] of approximately 3500 K, the lattice specific heat C_ℓ at 280 K can be estimated to be approximately 1 J/mol K. The same amount of normal-state $C_e = \gamma T$ would also prevail at 280 K if the coefficient $\gamma = 3.6$ mJ/mol K^2, which is comparable to that of many conventional superconductors.

The difficulty rests with the high-pressure aspect in calorimetric measurements. A standard pressure-cell approach was successfully employed on superconducting uranium some 50 years ago,[5] but only at 10 kbar. Researchers are designing and developing diamond anvil cells, but they face challenges regarding pressure limits and heat leak. However, as we look back, after 1911 it took more than 40 years of improving cryogenics and low-temperature calorimetry to finally reveal exponential-temperature dependence of C_{es}, which was important to the Bardeen-Cooper-Schrieffer theory. We now need to overcome another technical hurdle—in pressure instead of temperature.

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▶ **Pickett and Eremets reply:** X. H. Zheng and J. X. Zheng focus on McMillan's classic 1968 paper to address the decades-studied but unresolved question of maximum T_c. The last short section of his paper was on issues of maximum T_c. Though he carefully stated that his equation for T_c "was derived for $\lambda \lesssim 1$," he nevertheless extrapolated

from it to consider possibilities for higher, and maximum, T_c. He recognized that λ and ω (the coupling strength and characteristic frequency) were coupled via the relation $\lambda = \eta/M\omega^2$ in terms of the McMillan–Hopfield electronic stiffness η (more often referred to as the Hopfield parameter), which indicates that λ and ω are strongly intertwined. Within a class of similar materials, it was conjectured, η might be considered to change very little, so one might consider T_c (η,λ) without explicit dependence on ω. Conversely, one might consider T_c (η,ω). That approximation of constant η has been found, over the years, to be poor in several classes of materials, including hydrides.[1]

But having supposed that, McMillan reported that extrapolation of his equation outside the range of derivation indicated a broad maximum around $\lambda = 2$, or $\omega^2 = \eta/2M$. Studies conducted a few years after McMillan's, by Philip Allen and Robert Dynes,[2] established rigorous results, but their relevant result here is that the McMillan equation is *not* accurate around $\lambda = 2$ or greater (unlike the claim by Zheng and Zheng).

It is widely understood, as pointed out by McMillan and again by Zheng and Zheng, that any "maximum T_c" is material class dependent.

We do not recommend using any T_c equation beyond that of Allen–Dynes to give realistic values of T_c, given the necessary input.

Jim Ho has emphasized the important role that the specific heat $c_V(T)$ continues to play in the understanding of superconducting properties. In 1957, $c_V(T)$ data recorded every 2–3 degrees,[3] and tabulated but not plotted, just missed showing the structure in $c_V(T)$ near 40 K in magnesium diboride that would have led to the discovery of its paradigm-breaking superconductivity. Instead it remained hidden until its discovery[4] in 2001. Specific heat is a crucial probe in the understanding of low-temperature superconductivity and of system changes as the superconducting state is entered.

Even in MgB_2, with T_c ~ 40 K, the signal in $c_V(T)$ at T_c is small because the lattice contribution grows so much more rapidly than the electronic contribution. In hydrides at T_c of 200–260 K, the signal relative to the lattice specific heat will be smaller still. Ho suggests that it may still be observable. More to the point, and recognized by Ho, the diamond anvil cells that are necessary to study very high pressure require a cell of size and mass orders of magnitude greater than the sample, so the signal due to the sample is difficult to obtain. Researchers have measured $c_V(T)$ to pressures[5] of 10 GPa, but the challenges in extending such measurements to the 200 GPa range are considerable.

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