Comment on "Low-temperature phonon thermal conductivity of single-crystalline Nd_2CuO_4: Effects of sample size and surface roughness"

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In this Comment, we show that the experimental data reported by Li *et al.* [Phys. Rev. B **77**, 134501 (2008)] do not support the phonon specular reflection at low temperatures for high-T_c cuprates because the phonon mean free path ℓ calculated from their thermal conductivity data is much smaller than the averaged sample width above ~100 mK for both Nd_2CuO_4 and $YBa_2Cu_3O_{6.0}$ single crystals.

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In a recent paper, Li *et al.*[1] reported their low-temperature thermal conductivity (κ) studies on Nd_2CuO_4 single crystals. Based on their examinations of the effect of sample size and surface roughness on the phonon heat conductivity κ_p, they concluded the dominance of specular phonon reflection in high-T_c cuprates and proposed an empirical power law $T^{\alpha}(\alpha<2)$ to describe κ_p/T. They further used this empirical formula to reanalyze our published data[2] for Zn-doped $YBa_2Cu_3O_y$ (YBCO) and claimed that the universal thermal conductivity of *d*-wave quasiparticles at $T\rightarrow 0$ was confirmed. In this Comment, we show that both their experiments and data analysis are problematic or self-inconsistent, and therefore their conclusion on our data of Zn-doped YBCO lacks reasonable ground.

Li *et al.*[1] showed that the thermal conductivities of a wide Nd_2CuO_4 sample and a narrow one (cut from the wide sample) differ, as did the thermal conductivities of an as-grown sample and the same sample after surface roughening, and claimed that the observed differences support their assertion that phonons are in the boundary scattering regime below 0.5 K and that the specular reflection off sample surface is important, causing the $T^{\alpha+1}(\alpha<2)$ dependence of κ in a rather broad temperature range. Let us first point out that, contrary to what Li *et al.* claimed, the phonons are *not* really specularly reflected in their samples by correctly calculating the phonon mean free path ℓ from their data and comparing it with the averaged sample width W, which is usually taken to be $2/\sqrt{\pi}$ times the geometrical mean width $\bar{w}$.[3] Note that previous studies on the specular reflection unanimously found[4–6] that ℓ gets much longer than W when the specular reflection becomes important. Actually, since κ_p is equal to $\frac{1}{3}C\bar{v}\ell$, where $C=\beta T^3$ is the phonon specific heat and $\bar{v}$ is the averaged sound velocity, and both β and $\bar{v}$ are known experimentally for Nd_2CuO_4,[7–9] one can easily calculate ℓ in the samples of Li *et al.*[1] The coefficient β of Nd_2CuO_4 were reported to be about 0.42–0.50 mJ/mol K.[8,10] To avoid underestimating the value of ℓ, we choose $\beta=0.42$ mJ/mol K for the calculation. Another parameter, the averaged sound velocity, can be calculated by $\bar{v}=\Sigma_i v_i^{-2}/\Sigma_i v_i^{-3}$,[11] where i represents the three acoustic phonon modes. Here, we use the experimental values of the in-plane sound velocities of Nd_2CuO_4 from Ref. 9, $v_L=6050$ m/s, $v_{T1}=4220$ m/s, and $v_{T2}=2460$ m/s (which were also used by Li *et al.*[1]), to obtain $\bar{v}=2940$ m/s. Figure 1 shows the temperature dependence of ℓ calculated from the data in Ref. 1. One can see that for most cases ℓ only becomes comparable to W at the lowest temperature, and it stays much smaller than W in the temperature range where Li *et al.*[1] argued that the boundary scattering is taking place (below 0.5 K). For surface-roughened sample, ℓ is so small that it is much smaller than W even at the lowest temperature. Therefore, the magnitude of ℓ is obviously inconsistent with the assertion that phonons are boundary scattered below 0.5 K in Nd_2CuO_4. In fact, since $\kappa_p=\frac{1}{3}(\beta T^3)\bar{v}\ell$, a departure of κ_p from the T^3 dependence always comes from a T dependence of ℓ, and it occurs either when the specular reflection is important (which causes $\ell>W$) or when phonons are not in the boundary scat-

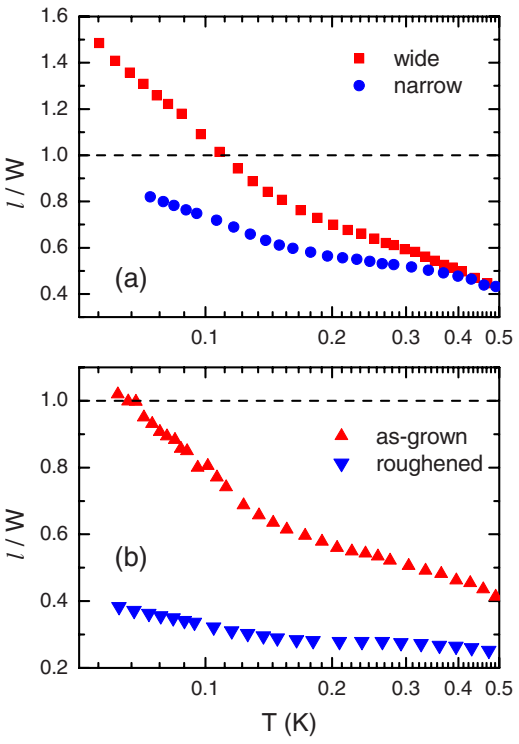

FIG. 1. (Color online) Temperature dependence of the calculated phonon mean free path ℓ divided by the averaged sample width W for Nd_2CuO_4. The raw data of κ are taken from Ref. 1.

tering regime (in which case $\ell < W$). Therefore, one can conclude that in Nd_2CuO_4 at temperatures higher than ~100 mK, phonons are not in the boundary scattering regime and the phenomenological $T^{\alpha+1}(\alpha<2)$ dependence comes from some additional scattering that only *reduces* ℓ.[12]

Furthermore, one can see that a comparison of the thermal conductivity data between the wide sample and the narrow one indicates some self-inconsistency if one tries to employ the specular reflection to explain the $T^{\alpha+1}$ dependence: when the sample is gradually cooled, one expects that ℓ gradually increases when the microscopic scattering is becoming less effective, and finally ℓ is equal to the averaged width, where the phonons enter the boundary scattering limit (about 0.5 K in the speculation of Li *et al.*). Upon further cooling, ℓ would become larger than the averaged width if the specular reflection is at work. Naturally, the characteristic temperature where ℓ is becoming comparable or equal to the averaged width should not strongly decrease with the sample size; rather, it should move to higher temperature upon decreasing the width. This is clearly opposite to what the data of Li *et al.* imply, as is demonstrated in Fig. 1(a). Another self-inconsistency appeared when Li *et al.*[1] compared the data between the as-grown sample and the surface-roughened one, that is, the two data sets differ by as much as a factor of 2 at 0.5 K where κ should already be mostly governed by microscopic scattering mechanisms, which should give a sample-size-independent thermal conductivity. (Here, we are not talking about thermal *conductance*.) This is clearly inconsistent with what they claimed.[1] Note that the cutting or sanding process could bring some cracks into the samples, and our own experience taught us that small cracks can easily be created when flux-grown crystals are cut; the narrower and thinner the sample, the more significantly the cracks affect the transport results.

It should be noted that Li *et al.*[1] showed an estimation of ℓ for the surfaced-roughed sample by using the following formula:

$$\kappa_p = \frac{2}{15}\pi^2 k_B \left(\frac{k_B T}{\hbar}\right)^3 \langle v^{-2}\rangle \ell, \tag{1}$$

in which only one parameter $\langle v^{-2}\rangle$ is necessary for the calculation. To obtain this formula, there is an approximation for the phonon specific-heat coefficient

$$\beta = \frac{2\pi^2}{5}\left(\frac{k_B^4}{\hbar^3}\right)^3 \left\langle \frac{1}{v^3} \right\rangle, \tag{2}$$

where $\langle \frac{1}{v^3} \rangle$ is the average of the inverse third power of the long-wavelength phase velocities of the three acoustic modes.[11,13] Calculating β with this approximation using measured sound velocities would be valid if the sound velocity solely reflects the dispersion of the acoustic phonon near the Γ point. However, Eq. (1) is apparently not precise when one compares the experimental results of β and the sound velocities:[8,9] using the experimental velocities from Ref. 9, one obtains β=0.20 mJ/mol K from formula (2), which is smaller than the experimental value of β(0.42–0.50 mJ/mol K).[8] In this sense, the calculation of Li *et al.* using formula (1) is not well supported by the experimental literature. Furthermore, their calculation[1] itself is problematic and ℓ is at least 30% overestimated: they used a roughly averaged value of the velocities ($\bar{v}$=4000 m/s) for calculating $\langle v^{-2}\rangle$ through $1/\bar{v}^2$(=6.25×10^{-8} s^2/m^2); however, one can easily notice that $\langle v^{-2}\rangle$ should be the averaged value of the inverse second power of the sound velocities of the three acoustic modes, which is $\langle v^{-2}\rangle$=8.29×10^{-8} s^2/m^2.

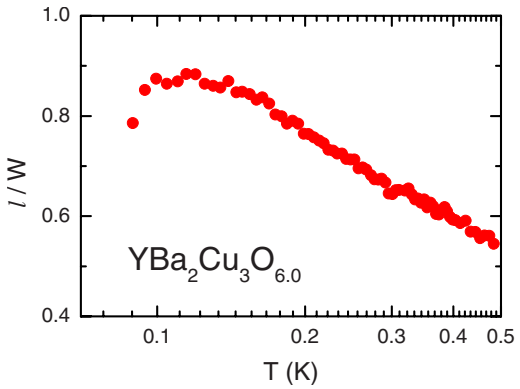

FIG. 2. (Color online) Temperature dependence of the calculated phonon mean free path ℓ divided by the averaged sample width W for $YBa_2Cu_3O_{6.0}$. The raw data of κ are taken from Ref. 3.

Therefore, the data of Li *et al.*[1] for Nd_2CuO_4 do not really support their speculation that the specular phonon reflection is important in cuprates. Then, what about another cuprate, YBCO, which they simply assumed to have the same phonon transport properties as Nd_2CuO_4? One can easily find the answer from the thermal conductivity data of an insulating YBCO sample with y=6.0, reported by the same group.[3] In Fig. 2, we show the temperature dependence of ℓ in this sample where the heat transport is purely phononic, using the data from Ref. 3. It is clear that the YBCO crystal shows a standard phonon transport behavior, with the boundary scattering limit only achieved below 140 mK, where ℓ is close to the averaged size and κ shows a T^3 dependence. Actually, it was already demonstrated[3] that the low-T κ/T data of this sample below 140 mK can be reasonably well fit to $a+bT^2$ with zero intercept (a=0).

Neglecting those circumstances, Li *et al.*[1] used the formula $\kappa/T=a+bT^{\alpha}$ to refit our low-T thermal conductivity data of the superconducting YBCO and Zn-doped YBCO (Ref. 2) and concluded that κ_0/T is unchanged upon Zn doping. Based on such an analysis, they claimed that our data confirm the universal thermal conductivity of d-wave quasiparticles for $T\rightarrow 0$. However, it must be pointed out that even if the phonon heat conductivity showed a $T^{\alpha+1}$ dependence, the fitting to $\kappa/T=a+bT^{\alpha}$ is meaningful *only when the electronic heat conductivity is a linear function of temperature*. In this regard, one should not forget an important fact, which was first reported by the Taillefer *et al.*,[14] that the electronic contribution to the heat transport in clean YBCO increases rapidly with temperature following a T^3 law due to the thermal creation of heat-carrying quasiparticles near the nodes. If one takes into account this T^3 dependence of the electronic term at $T\neq 0$, one can easily see that the analysis of our YBCO data by Li *et al.*[1] is obviously erroneous; in contrast,

our original fitting[2] with $\kappa/T=a+bT^2$ is robust against the appearance of the T^3 electronic contribution and, hence, is reliable for extracting the residual thermal conductivity. In fact, the "main effect" of Zn doping to cause a dramatic suppression of the *slope* of κ/T, which Li *et al.* noted in Ref. 1, is mostly due to the diminishment of this electronic T^3 term.

It would also be useful to note that Nd_2CuO_4 used in the work of Li *et al.* is not an ideal system for studying the purely phononic heat transport because of its complicated magnetism.[15] In fact, theoretically the Nd magnon modes are predicted to be effectively gapless in zero field,[15] so the conjecture of Li *et al.*[1] that the Nd magnons are gapped and do not contribute to the heat transport does not have any theoretical support. If the magnon contribution is not negligible in Nd_2CuO_4, the true mean free path of phonons would be even smaller than those shown in Fig. 1.

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[10] In Nd_2CuO_4, one cannot use very low-temperature specific-heat data for analyzing the phonon term because of the appearance of a magnetic peak, so in Ref. 8 the β value was obtained from the simple fitting of T^3 to the data at intermediate temperature. It is known that in the temperature range $0.02<T/\theta_D<0.1$ (θ_D is the Debye temperature), one had better use the low-frequency expansion of the Debye function, which gives $C_v=\beta T^3+\beta_5 T^5+\beta_7 T^7+\cdots$; [see the textbook by A. Tari, *Specific Heat of Matter at Low Temperatures* (Imperial College Press, London, 2003)]; This formula is commonly used for analyzing the phonon specific heat at this intermediate temperature range. [See, for example, the papers on the specific heat of La_2CuO_4; C. F. Chang, J. Y. Lin, and H. D. Yang, Phys. Rev. Lett. **84**, 5612 (2000); H. H. Wen, Z. Y. Liu, F. Zhou, J. Xiong, W. Ti, T. Xiang, S. Komiya, X. Sun, and Y. Ando, Phys. Rev. B **70**, 214505 (2004)]; It is important to recognize that the correction to the simple T^3 analysis can decrease the β value, but it can never change the β value by as much as a factor of two, as can be seen in these reference papers. More importantly, if the specific-heat data in the intermediate temperature range can still be well fitted to the simple T^3 law, which is actually the case for Nd_2CuO_4, it means that the higher-power terms are effectively negligible in this material. (In Ref. 8, the T^3 law fits the data well from $\sim$15 to 25 K or even higher temperature.) This is not surprising, because the higher-power term β_5 is usually found to be a small positive value in La_2CuO_4, but it can even be a small negative value in some other materials [e.g., see the data for Na_xCoO_2; Y. Ando *et al.*, Phys. Rev. B **60**, 10580 (1999)]; Also, it is useful to note that one can neglect the possibility that the β value determined at 15–25 K for Nd_2CuO_4 might be enhanced by a magnon contribution, because it is established that in the Néel state of Nd_2CuO_4, Cu magnons (which are the only possibility at 15–25 K) are gapped although it is still an open question whether the Nd magnons (which can only be relevant below 3 K) are gapped as well (Ref. 15).
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