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Surface specific heats of metal nanocrystals at low temperatures

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In order to quantitatively explain the enhanced specific heat of metal nanocrystals measured from 4.2K to 80K, an analytical expression has been deduced to determine the surface specific heat in nanocrystals, which is proportional to $T^{2.5}$ at low temperatures. The consequently calculated specific heat and surface Debye temperature of copper nanocrystals are in good agreement with the experimental data. This well explains why the experimental specific heat of copper nanocrystals is enhanced with respect to the bulk and exhibits a different feature as a function of temperature from that of the bulk at low temperatures. The first experimental evidence is presented that the effectively spatial dimension of surfaces should be between 2D and 3D, neither pure 2D nor 3D due to the effect of atoms in the core of nanocrystals.

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1. Introduction

Nanomaterials display novel and often enhanced properties with respect to the bulk materials, which drive the pure science to explore the background mechanism and open up possibilities for new technological applications. The specific heat of metal nanocrystals has been revealed to be enhanced in comparison with the bulk crystals at low temperatures due to the presence of surfaces, interfaces, or grain boundaries [1-8]. The Debye's T^3 law, which is very efficient to describe the specific heat of the three-dimensional high-symmetry bulk crystals, is often applied to explain the enhanced specific heat of nanocrystals [7, 8]. Although it is qualitatively successful for the nanocrystals, the Debye's T^3 law cannot be self-consistent in quantitatively explaining both the enhanced low-frequency vibrational density of states (VDOS) of nanocrystals and the variation of their specific heat with temperature [1-8]. It always gives the phonon specific heat as $\sim T^3$ at low temperatures while the VDOS of nanomaterials at low frequencies is a power law of frequency with an exponent below 2 due to the existence of the surfaces, interfaces, or grain boundaries [8-14]. The fit of the low-temperature specific heat of nanocrystals on the basis of the Debye's T^3 law results in a much smaller surface Debye temperature than the experimental data [8]. The size-dependent Debye temperature is deduced to explain the enhanced specific heat within the framework of the Debye's T^3 model [15]. Some studies have used the Einstein model to explain the enhanced specific heat of small metal nanocrystals at low temperatures [16, 17]. Some studies made a polynomial form to fit the experimental specific heats and revealed the drawback of the Debye's T^3 model for nanocrystals [16]. Although the specific heat of nanocrystals can be mathematically fitted as a polynomial function of temperature expanding from 0 to n-order power law of T in the framework of Taylor series, the physical meaning of each term in this polynomial function is not clear.

The surfaces are generally assumed to be two-dimensional (2D) and thus their phonon specific heat is determined to obey the $\sim T^2$ law at low temperatures, which achieves the specific heats of the solid with surfaces strikingly deviating from the experimental data at low temperatures [18]. It is still controversial whether the VDOS at low frequencies depends linearly or nonlinearly on

frequency for the surfaces, interfaces or grain boundaries in nanomaterials [9-14]. These studies imply that the surfaces may not possibly be 2D, between 2D and 3D [9-11]. Up to now, there is no self-consistent description of the relationship among the enhanced specific heat at low temperatures, the VDOS at low frequencies, and the surface Debye temperature of metal nanocrystals [7]. There is also no well-established intuitive explanation for the enhancement in the specific heat of nanocrystals [7]. It is our purpose to quantitatively determine the effect of surfaces on the specific heat of nanocrystals at low temperatures. By combining the experimental measurement and theoretical analysis, the surface phonon specific heat at low temperatures is deduced as function of temperature ($\sim T^{2.5}$) and the spatial dimension of surfaces is suggested to be between 2D and 3D, neither pure 2D nor 3D due to the effect of atoms in the core on surfaces of nanocrystals. The calculated specific heat and surface Debye temperature of Cu nanocrystals at low temperatures are shown to agree well with the experimental data.

2. Experiments

Cu nanoparticles were firstly produced by the flow-levitation method under the protection of Ar gas to prevent them from oxidation as described in Refs. 19 and 20. In this way, all the Cu nanoparticle are almost spherical. They were then compacted at 300K in vacuum still under the protection of Ar gas to form a $\Phi 5\text{mm} \times 1\text{mm}$ disc of nanocrystals. Nanocrystals is so loosely packed that the surface effect can be discriminated. Their structures were characterized by a Philips Xpert Pro MPD X-ray diffractometer (XRD) with the Cu $K\alpha$ ($\lambda=1.5406 \text{ \AA}$) radiation and a S440-type scanning electronic microscope (SEM). The specific heat of Cu nanocrystals was measured in a Quantum Design PPMS in the temperature range of 4.2K-80K. The bulk Cu (coarse-grained Cu) was also analyzed for comparison.

Fig.1 shows the XRD spectra and SEM images of the Cu bulk and nanocrystals. It can be found from the XRD spectra that Cu nanocrystals have the same face-centered cubic (fcc) structure as the bulk and that there is no peak related to copper oxide in the XRD spectra of the bulk and nanocrystals. The SEM images indicate that the grain size, the porosity, and the density in

nanocrystals are much smaller, much higher, and much lower than those in the bulk, respectively. The SEM image also shows spherical-shape grains in nanocrystals. Considering the spot size of X rays incident on the sample, the regime in the bulk analyzed by the XRD may prefer to a quasi-single-crystalline texture for the X-ray diffraction intensity from the high-index planes relative to the one from the (111) planes is weaker than nanocrystals, in which multiple grains with different orientations contribute to the X-ray diffraction.

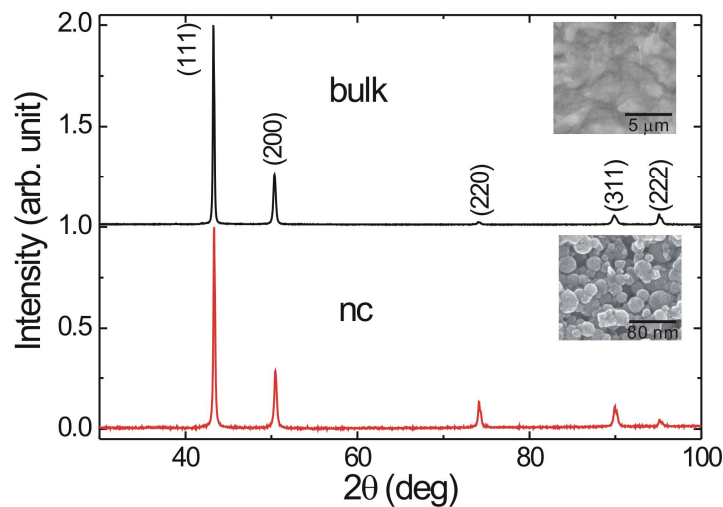


Fig.1 (Color online) The XRD patterns of Cu nanocrystals (nc) and the bulk with their SEM images in the insert. The intensity of each diffraction peak has been normalized to the one from the (111) planes.

The average grain size in Cu nanocrystals is estimated as 45nm in diameter (d) from the XRD patterns and SEM images in Fig.1, much smaller than the ones in the bulk Cu. Theoretically, when the distance between two atoms is larger than about 1nm, their interaction potential tends to zero [21, 22]. Experimentally, the thickness of the surfaces (δ) is commonly assumed as 1nm [1, 8]. These atoms are thus determined as the surface ones when they are within this distance (1nm) from the outmost and the others as the core or volume atoms. Therefore, the surface-to-volume atom ratio (α) can be estimated as $\alpha=3\delta/d=6.6\%$ in the prepared nanocrystals.

The specific heats of the Cu bulk and nanocrystals have been measured from 4.2K to 80K and are plotted in Fig.2 as a function of temperature. It is evident that the specific heat of nanocrystals is

enhanced with respect to the bulk. The specific heat of a bulk metal contains the contribution from both electrons and phonons, which can be well described according to the free electron model and the Debye's model to be proportional to T and T^3 , respectively [23]. For Cu, the phonon specific heat is much larger than the electron specific heat when the temperature is above 4K. Therefore, the present specific heat measured from 4.2K to 80K results mainly from the lattice vibrations in the Cu bulk and nanocrystals.

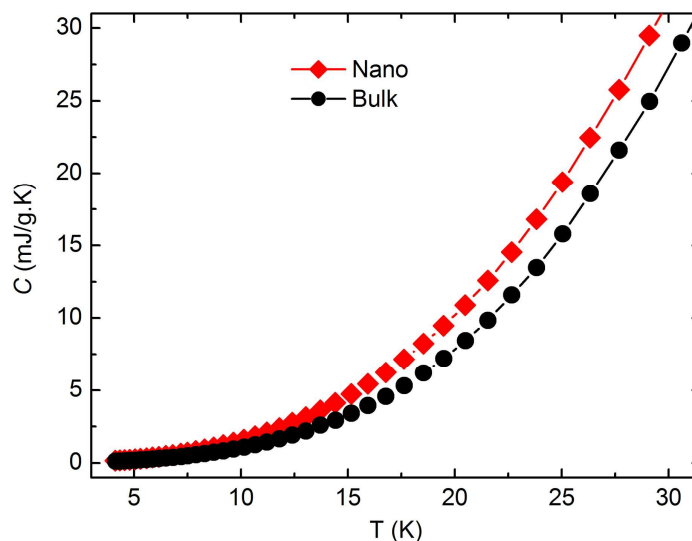


Fig.2 (Color online) The specific heat of the Cu bulk and nanocrystals as a function of temperature experimentally measured from 4.2K to 80K.

Compared with the counterpart of the bulk, the specific heat of nanocrystals is enhanced at a fraction larger than 2.5% from 4.2K to 80K (see Fig.3), higher than the measurement sensitivity of PPMS (about 2%). The enhancement fraction is even higher than 10% below 30K with a peak at 10K. Our previous studies indicate that the volume specific heat in nanocrystals should obey the Debye's T^3 law as the bulk. This confirms that the enhancement of specific heat is indeed due to the surface effect, not to the measurement error.

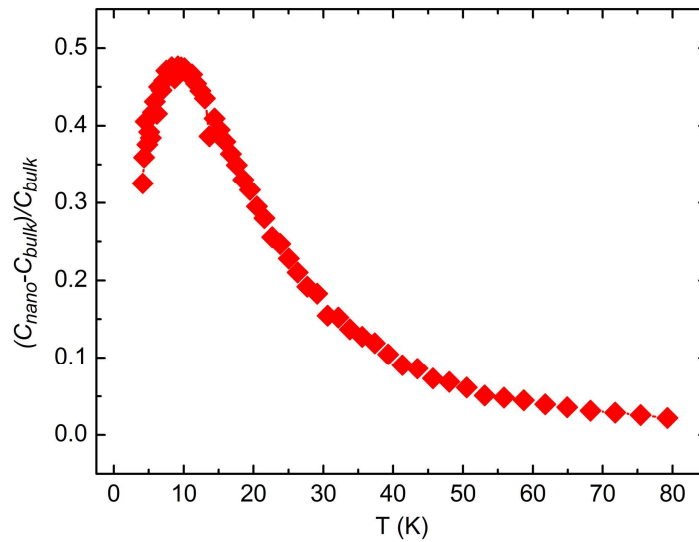


Fig.3 (Color online) The enhanced fraction in the specific heat of Cu nanocrystals as a function of temperature experimentally measured from 4.2K to 80K.

3. Theoretical Analysis and Discussion

In order to understand the experimental results, nanocrystals are divided into surface and core atoms. Consequently, the total specific heat of nanocrystals is given by

$$C(T) = \gamma T + \alpha C_s(T) + (1 - \alpha) C_v(T) \quad (1)$$

Where γ is the Sommerfeld coefficient of the electronic contribution [23], and C_s and C_v are the phonon specific heats of surface and core atoms in the nanocrystal, respectively. α is equal to zero for the bulk. The phonon specific heat is generally calculated by [23]

$$C_{phonon}(T) = 3R \int x^2 \frac{e^x}{(e^x - 1)^2} g(\omega) d\omega \quad (2)$$

Where R is the gas constant, $g(\omega)$ is the VDOS at the frequency of ω , $x = \hbar\omega/k_B T$, \hbar is Planck's constant, and k_B is Boltzmann's constant. Therefore, the phonon specific heat can be theoretically obtained if $g(\omega)$ is known. The previous studies have shown that the surface VDOS is scaled as $g(\omega) \sim \omega^{1.5}$ and the core VDOS as $g(\omega) \sim \omega^2$ at low frequencies [9-11, 24]. This implies the spatial dimension $n=2.5$ for surfaces and $n=3$ for the core. This viewpoint implies that the surfaces are neither pure two dimensional (2D) nor pure three dimensional (3D). We argue that the surfaces in

the nanocrystals or in the bulk with free surfaces must “feel” the effect of atoms in the core (3D) and thus be endowed with, more or less, both 2D and 3D features. This is different from the pure 2D system. In this sense, the spatial dimension of surfaces should be between 2D and 3D [9-11]. Meanwhile, the vibrations at low frequencies are expected to be long-wavelength acoustic phonons. Since we will consider the phonon specific heat at low temperatures below 80K, the contribution of high-frequency optical phonons is weak and thus neglected [23]. The previous theoretical and experimental studies have also demonstrated that the specific heat could be obtained reliably from even a low-frequency approximation to the VDOS [25]. Therefore, following the framework of the Debye model, the distribution of the phonon frequencies at low temperatures is then given by

$$g(\omega) = \frac{n\omega^{n-1}}{\omega_D^n} \text{ for } \omega \leq \omega_D \quad (3)$$

$$g(\omega) = 0 \text{ for } \omega > \omega_D \quad (4)$$

and

$$\int_0^\infty g(\omega)d\omega = 1 \quad (5)$$

Where n denotes the spatial dimension and can be either an integer or a fraction. The limiting angular frequency ω_D still defines the Debye temperature, θ_D , as $\theta_D = \hbar\omega_D/k_B$.

An introduction of Eq.(3) into Eq.(2) results in an analytical expression for the phonon specific heat, which depends explicitly on temperature, Debye temperature, and the spatial dimension n ,

$$C_{phonon}(T) = 3nR \left(\frac{T}{\theta_D} \right)^n \int_0^{\theta_D/T} \frac{e^x}{(e^x - 1)^2} x^{n+1} dx \quad (6)$$

Especially, at low temperatures, Eq.(6) reduces to

$$C_v(T) = \frac{12\pi^4}{5} R \left(\frac{T}{\theta_D^v} \right)^3 \quad (7)$$

for the bulk and the core of the nanocrystal, and

$$C_s(T) = \frac{211\pi^{1/2}}{8} R \left(\frac{T}{\theta_D^s} \right)^{2.5} \quad (8)$$

for the surfaces of the nanocrystal. Here θ_b^v is the bulk Debye temperature and θ_b^s the surface Debye temperature. It is worth noticing that Eq.(7) is actually the Debye's T^3 law for the specific heat of a solid at low temperatures.

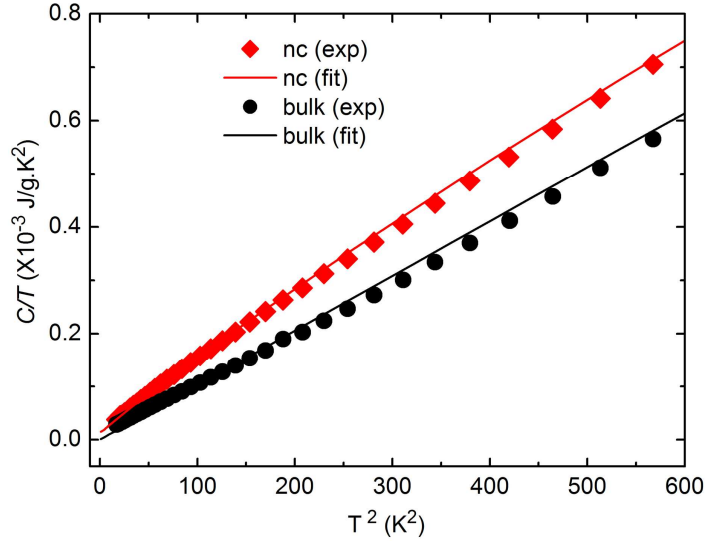


Fig.4 (Color online) The specific heat C of Cu nanocrystals and the bulk at low temperatures. The C/T is plotted versus T^2 . The symbols are the experimental data and the curves are the fitted results based on Eqs.(1), (7) and (8).

On the basis of Eqs.(1), (7), and (8), the least-squared fit generates a curve well matching the experimental data for the bulk and for the nanocrystals, respectively. The surface electronic specific heat is found to be a bit smaller than the bulk electronic one. At this point, we will carry out further experimental measurement in the future at low temperatures below 4K, when the electron specific heat is more significant than the phonon one. A comparison between the C/T versus T^2 plots of the Cu nanocrystals and the bulk at low temperatures is shown in Fig.4. It is obvious that the specific heat of nanocrystals exhibits a different variation feature with temperature from that of the bulk. The bulk Debye temperature is thus obtained as $320\text{K} \pm 10\text{K}$, in good agreement with those reported for the bulk Cu [23]. It is also found that the surface Debye temperature is smaller than the bulk Debye temperature due to the phonon softening at surfaces. The surface Debye temperature is obtained as $225\text{K} \pm 10\text{K}$ here, in accordance with the experimental values of 210K for (100) and

244K for (111) surfaces [26]. The fit of the low-temperature specific heat of Cu nanocrystals using the Debye's T^3 law obtained a surface Debye temperature (152K) for the Cu nanocrystals, much smaller than the experimental data [26]. This fact confirms that surfaces can not be treated as 3D and the Debye's T^3 law is invalid in describing the surface specific heat. The present analysis is reasonable in evaluating the surface specific heat by assuming the spatial dimension of surfaces as $n=2.5$. Since the phonon specific heat of the core in nanocrystals obeys the Debye's T^3 law with the same Debye temperature as that of the bulk, it is indeed the surfaces who contribute to a higher low-temperature specific heat in nanocrystals than in the bulk, as revealed by the previous studies [1-8]. Although the grains in Cu nanocrystals have actually a size distribution and a different size must change the surface-to-volume atom ratio, the $T^{2.5}$ dependence of the surface phonon specific heat is always solid and the whole surface-to-volume atom ratio of nano Cu is statistically equivalent to the one of the average-size grains.

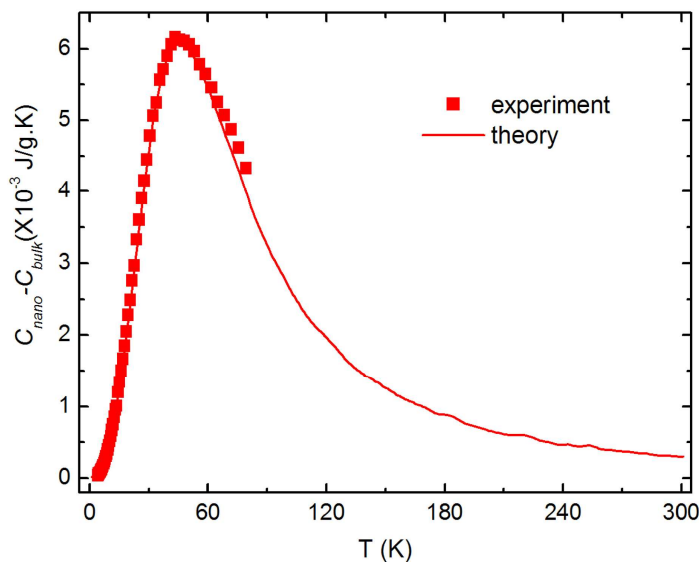


Fig.5 (Color online) The excess specific heat of Cu nanocrystals as a function of temperature. The symbols are experimental data and the curve is the calculated result based on Eqs.(1), (7) and (8).

Fig.5 shows the excess specific heat of Cu nanocrystals relative to the counterpart of the bulk as a function of temperature. A main feature in Fig.5 is that the excess specific heat reaches the maximum at about 50K, which has been confirmed by the molecular-dynamics simulations [25]. It

is evident that the variation of the excess specific heat of nc Cu with temperature calculated according to Eqs.(1), (7), and (8) agrees with the experimental measurements. As a matter of fact, the surface effect has been revealed to be responsible for the enhanced low-frequency vibration mode and thus the enhanced specific heat of nanocrystals at low temperatures [3-14]. With increasing the grain size in nanocrystals, the fraction of atoms at the surfaces decreases and result in a less contribution of surface phonons to the total specific heat as indicated in Eq.(1). Consequently, the specific heat of nanocrystals with larger-size grains is closer to the one of the bulk. This may be the reason why the excess specific heat of nanocrystals decreases with increasing the grain size as revealed by the other studies [3].

4. Conclusion

In conclusion, we have deduced an analytical expression to describe the surface specific heat in nanocrystals in order to quantitatively explain why the low-temperature specific heat of Cu nanocrystals exhibits a different variation feature with temperature from that of the bulk and why it is enhanced with respect to the bulk. Especially, the surface phonon specific heat C_s at low temperatures is proportional to $T^{2.5}$, not to T^3 as that for the bulk. This presents the first experimental evidence that the spatial dimension of surfaces should be between 2D and 3D, neither pure 2D nor 3D due to the effect of atoms in the core on surfaces of nanocrystals. The calculated specific heat and surface Debye temperature of Cu nanocrystals are in good agreement with the experimental data at low temperatures. Although only the surface specific heat in this report is deduced as a function of temperature, the relationship of $C_s \sim T^{2.5}$ is expected to be popularized into the other similar defects such as interfaces and grain boundaries in nanocrystalline materials except for a possibly different Debye temperature. Lastly, it should be mentioned that the calculated specific heat would gradually deviate from the real value with increasing temperature for the present relationship of $C_s \sim T^{2.5}$ is simply based on the $g(\omega) \sim \omega^{n-1}$ at low frequencies and neglects the contribution of high-frequency optical phonons.

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