

Two-Dimensional Thermodynamic and Magnetic Properties in Copper Nanocrystals

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Due to the negligible amount of surface mass in bulk materials, it is almost not feasible to directly measure the surface macroscopic properties such as specific heat and magnetic susceptibility. Whereas if materials are fabricated in the form of ultra fine particles with the size in the order of a few tens of angstroms to a couple of hundreds of angstroms, their surfaces can be considerably increased and their physical properties can be delineated. In this work we performed the measurements of low temperature specific heat for $T = 0.3 - 20$ K and magnetic susceptibility for $T = 1.8 - 300$ K of both bulk copper and Cu nanocrystals with an average particle size around 500 \AA . It is found that the specific heat and magnetic susceptibility of Cu nanocrystals are much larger than those of bulk copper. The specific heat and magnetic susceptibility of Cu nanocrystals exhibit the characteristics of two dimensional conduction electrons and lattice phonons which are associated with the surface area, electron density of states and probably with the defects, disorders and inter-grain boundaries in Cu nanocrystals.

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I. INTRODUCTION

Lately due to the more novel properties gradually discovered in nanocrystals [1], such materials have drawn more attentions of scientists and engineers [2]. The novel properties include unusually higher diffusivity and reactivity, more ductile behavior, larger thermal expansion and more significant specific heat and magnetic susceptibility as compared with those of coarse crystalline materials. Nowadays these novel characteristics are widely incorporated into new alloys which exhibit structure-related mechanical properties or which is

not existing owing to insolubility or low solubility of their constituent elements. Although a variety of physical properties of nanocrystalline materials are extensively studied and have been successfully applied to engineering applications, the properties in thermodynamic aspect have seldom been deliberately inspected, especially in the low temperature region. Usually the size of nanocrystal is in the order of a few ten angstroms to a couple of hundred angstroms. This exceptionally small size makes it to have larger surface fraction than that in bulk material, in other words nanocrystal carries larger atomic surface/volume ratio. For example, a spherical nanocrystal with diameter of 5 nm and atom size of 5 Å, the atomic surface/volume ratio is 6×10^{-4} . For a nanocrystal with size around 50 Å the atomic surface/volume ratio is up to 6×10^{-1} , which is about three orders larger than that of the former. Since nanocrystals generally are synthesized in inert gases by means of quick gas condensation, there is unavoidably creation in some extent of micro-grains, defects, disorders and inter-grain boundaries in nanocrystals for different materials [3]. The novel thermodynamic and magnetic properties related to these sophisticated structures and vast surfaces will be worthy of study.

II. EXPERIMENTAL DETAILS

To measure the specific heat of bulk copper a couple of $2 \times 2 \text{ mm}^2$ cross section and 0.8 mm thickness copper segments were cut from an ingot of copper metal with 99.9999% purity commercially available from Johnson Matthey. To prepare Cu nanocrystal specimens, about 20 mg of nanocrystal powders with average size around 500 Å bought from Vacuum Metallurgical Co., Ltd. were compacted and then compressed to about the same size as those of bulk copper samples. In order to examine the influences on physical properties of Cu nanocrystals by possible copper oxidation on their surface layers, a few pieces of Cu nanocrystal specimens were thermally annealed in H_2 atmosphere at 50 °C and 200 °C, respectively, for one hour for later comparison experiments. The crystal growth temperature for Cu nanocrystals is about 100 °C as reported in the literature [1].

The low temperature specific heat measurements were performed using a thermal-relaxation micro-calorimeter. The sample with one side being mirror-polished for good thermal contact and wiped with -50 microgram of Wake Field grease was attached to a sapphire holder on which a germanium thin film thermometry and a nickel-chromium heater were evaporated for temperature recording and heating power. The addenda was then semi-adiabatically isolated from bath by four gold-copper alloy wires [5] for thermal relaxation operation and electrical connections. By recording the time constant τ of temperature relaxation after cutting off the input of heating power, the specific heat of specimen can then be measured by $C = k\tau$, where k is the thermal conductance of link wires. The background of addenda and grease was properly subtracted based on a separate measurement. The

relative precision and the absolute accuracy of the calorimeter are confirmed within -2% and ~4%, respectively, by measuring a copper standard.

Measurements of magnetic susceptibility were implemented in a Superconducting Quantum Interference Device (SQUID) which was calibrated with a palladium standard before these measurements. To avoid to saturate the magnetization of specimens a prior magnetic field scan at 10 K was performed before each measurement to insure the proper choose of magnetic field. The X-ray spectra were taken by a rotating anode X-ray diffractometer of MAC. The precision of lattice constant determination is about 0.03% which makes it capable of solving 0.1% difference of lattice constants met in this task.

III. RESULTS AND ANALYSIS

Usually the specific heat of ordinary three-dimensional metal can be presented by the formula

$$C(T) = \gamma T + \beta T^3, \quad (1)$$

where

$$\gamma = D(\varepsilon_F) K_B^2, \quad (2)$$

and

$$\beta = 234 \frac{N K_B}{\Theta_{buk}^3}. \quad (3)$$

The first term of Eq. (1) is the specific heat of conduction electrons and the second term is the specific heat of the phonons. $D(\varepsilon_F)$ is the electron density of states at Fermi level, K_B is the Boltzman constant, N is the total number of atoms and Θ_{buk} is the Debye temperature of phonons in bulk. As mentioned above higher atomic surface/volume ratio and the existence of inter-grain boundaries in nanocrystals are so large that the specific heats of two-dimensional phases are remarkable. Theoretically the twodimensional specific heats [5] can be represented by

$$C_{2d} = \alpha T + \eta T^2, \quad (4)$$

where

$$\alpha = \frac{\pi L^2 m_e K_B^2}{3 \hbar^2}, \quad (5)$$

and

$$\eta = 239.86 \frac{T^2}{\Theta_{D2}^2}. \quad (6)$$

The first term is the specific heat of two-dimensional conduction electrons, the second term is the specific heat of twodimensional phonons, L^2 is the surface area and Θ_{D2} is the two-dimensional Debye temperature which is assumed to be approximately equal to surface Debye temperature 227 K obtained by LEED [6]. The specific heat of two-dimensional electrons is a linear function of temperature, the same form as that of three-dimensional electron gas. In contrast to the three-dimensional electrons, the specific heat of two-dimensional electrons is proportional to the surface area and is not dependent on the density of states.

It is supposed that the specific heat can be represented by Eq.

$$C(T) = aT + bT^2 + cT^3. \quad (7)$$

The first term is assumed to be the sum of specific heat of bulk electrons and surface electrons, the second term is supposed to be the specific heat of surface phonons and the third term as usual is treated as the specific heat of bulk phonons. If we fitted the specific heat data directly into polynomial Eq. (7), large uncertainties of coefficients a , b and c will occur due to too many variables and scattering in data. Since T^2 and T^3 terms have less weight in the low temperature region, we fitted Eq. (7) using data below 5 K to obtain less scattered linear temperature coefficients of $a(50081 \text{ Cu}) = 1.03 \times 10^{-3} \text{ J/K}^2 \text{ mol}$, $a(50^\circ\text{C annealed Cu nanocrystal}) = 1.0 \times 10^{-3} \text{ J/K}^2 \text{ mol}$, $a(200^\circ\text{C annealed Cu nanocrystal}) = 0.92 \times 10^{-3} \text{ J/K}^2 \text{ mol}$ and $a(\text{bulk Cu}) = 0.68 \times 10^{-3} \text{ J/K}^2 \text{ mol}$. The specific heats of copper oxide and the direct measured specific heats of bulk copper, Cu nanocrystals and two Hz-annealed Cu nanocrystals are shown in Fig. 1. Each curve of specific heat is least square fitted to Eq. (7) with determined coefficient “ a ” for each specimen. The coefficients of polynomials and the physical parameters thus obtained for the four specimens are listed in Table I. The coefficients of bulk copper are in good agreement with the data reported in the literature [4]. Since no quadratic term should be seen in bulk copper, the magnitude of coefficient $-0.01 \text{ mJ/K}^3 \text{ mole Cu}$ in quadratic term can be treated as the uncertainty of experimental data which is relatively small as compared with the corresponding coefficients $0.32 \text{ mJ/K}^3 \text{ mol}$ for $\text{Cu}(500 \text{ \AA})$, $0.29 \text{ mJ/K}^3 \text{ mol}$ for $\text{Cu}(50^\circ\text{C annealed})$ and $0.24 \text{ mJ/K}^3 \text{ mol}$ for $\text{Cu}(200^\circ\text{C annealed})$. The performance of our calorimeter and the applicability of the statistical fitting method are confirmed. The linear coefficient of specific heat of Cu nanocrystals is 1.03 mJ/K^2 , which is about 51% larger than that of bulk copper. The coefficient “ a ” monotonously decreased toward the value of bulk copper after the nanocrystal samples here annealed at 50°C and further annealed at 200°C . This trend is also roughly followed in the coefficients “ b ” and “ c ” of Cu nanocrystals within the uncertainty of data $\pm 2\%$. Based on a schematic sketch of a spherical copper nanocrystal and the lattice constant 3.63 \AA evaluated from X-ray diffraction spectra, the atomic surface/volume ratio is 0.022 and the total outer surface area per mole of copper nanocrystals is $8 \times 10^6 \text{ cm}^2$. Although the manufacturer fabricated these nanocrystals with

a lot of caution in preventing from possible oxidization, the oxidization is still possible in Cu nanocrystals. Since three-dimensional phonon of CuO is much larger than that in Cu, see Fig. 1 and Table I, the copper oxide contained in Cu nanocrystals is estimated to be about 3 – 5% by the difference of coefficient c' s in Cu nanocrystals and CuO. This values are much larger than the calculated surface atom occupation 2.2% and makes it possible that the copper oxidation exists in the interior of Cu nanocrystal. The uncertainty in the estimation of CuO is due to the difficulty in knowing the actual amount of specific heat originated from other sources such as inter-grain boundaries, defects disorders etc. If the difference in quadratic terms of specific heat of Cu nanocrystals and 200 °C Hz-annealed Cu nanocrystals is related to the surface diminishment by crystal growth and reduction at 200 °C Hz-annealing, applying Eq. (6) the outer surface area is estimated as $\sim 7 - 9 \times 10^6 \text{ cm}^2$ which approximately matches the expected value of $8 \times 10^6 \text{ cm}^2$ if the surface roughness

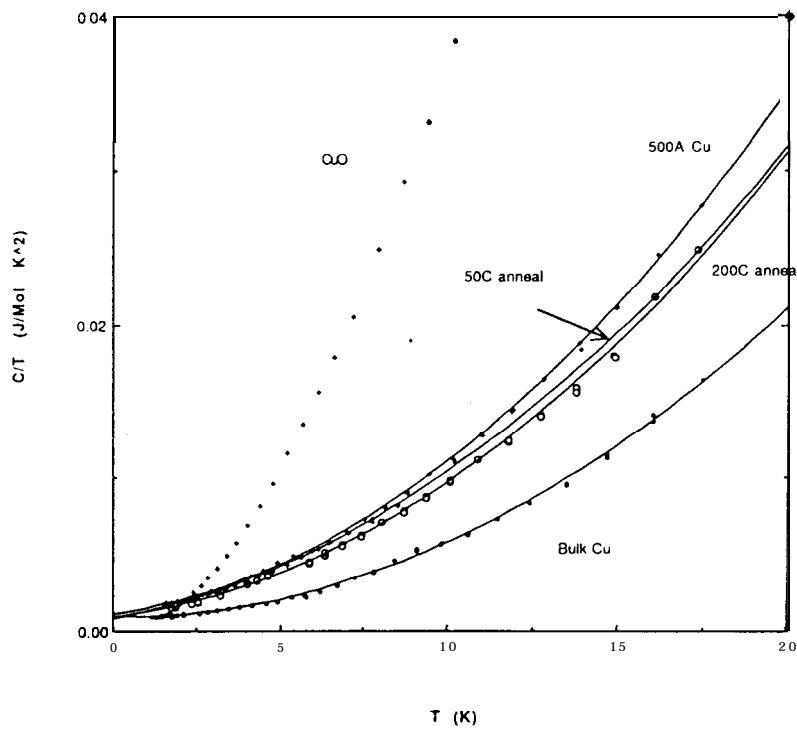


FIG. 1. C/T vs. T for CuO, 50 °C Hz-annealed Cu nanocrystals, 200 °C Hz-annealed Cu nanocrystals and bulk copper.

TABLE I. The temperature coefficients of specific heat in the polynomial $C(T) = aT + bT^2 + cT^3$ and the Debye temperatures as derived for CuO, Cu nanocrystals, 50 °C Hz-annealed Cu nanocrystals, 200 °C Hz-annealed Cu nanocrystals and bulk copper.

Sample	a (mJ/K ² mol Cu)	b (mJ/K ³ mol Cu)	c (mJ/K ⁴ mol Cu)	Θ (K)
500 Å Copper Nanocrystals	1.03	0.32	0.066	309
50 °C Hz-annealing Cu nanocrystals	1.00	0.29	0.068	305
200 °C Hz-annealing Cu nanocrystals	0.92	0.24	0.063	313
Bulk copper	0.68	0.01	0.051	336
Copper oxide	–	–	0.41	168

is considered in practical situation. In contrast to the result assuming the difference in linear terms of specific heats of Cu nanocrystals and 200 °C Hz-annealed Cu nanocrystals is associated with the specific heat of surface electrons in Eq. (5), a similar calculation showed that the surface area is $7 \times 10^7 \text{ cm}^2$ which is about 10 times larger than the value quoted above. This implies that about 90% of the specific heat calculated from the difference of linear term might be belonged to other sources such as electron density of states, inter-grain boundaries, defects and disorders in Cu nanocrystals. This presumption is supported by the result of 200 °C Hz-annealed Cu nanocrystals in which the linear coefficient is still very larger than that of bulk copper although 200 °C Hz-annealed Cu nanocrystals were already transformed to bulk-like form by their appearance of metallic surfaces.

A similar consequence exists in calculations of magnetic susceptibility data. The measurements of magnetic susceptibility of bulk copper, Cu nanocrystals and two H₂-annealed nanocrystals are shown in Fig. 2. The result shows that the bulk copper is diamagnetic and temperature independent as expected. The magnetic susceptibility of Cu nanocrystals and its thermally annealed counterparts are positive and almost temperature independent for $T > 100 \text{ K}$ but at lower temperatures Curie-Weiss like $X = C/(T + \theta)$ upturns, indicating the appearance of paramagnetic impurities. To extract the Curie

constants and Curie-Weiss temperatures the linear fits for inverse magnetic susceptibility vs. temperature shown in Fig. 3 and the related parameters derived are tabulated in Table II. The Curie constant and Curie-Weiss temperature are estimated as $C = 4.38 \times 10^{-4}$ emu and $\theta = 13.8$ K for Cu nanocrystals. The 50 °C Hz-annealed Cu nanocrystals shows a slightly smaller Curie constant and a similar Curie-Weiss temperature $\theta = 13.3$ K; a consequence of typical thermal annealing. Although 200 °C Hz-annealed Cu nanocrystals show an even smaller Curie constant, a right trend of thermal annealing but a much smaller Curie-Weiss temperature 1.6 K is derived which is comparable with 2.47 K for bulk copper. This result assures the assumption that the 200 °C Hz-annealed nanocrystals are already transformed to bulk-like copper. Since the paramagnetism of CuO is even weaker than that of Cu nanocrystals, this makes it difficult to estimate of oxidation by Curie constant of Cu nanocrystals. However, the magnitudes of magnetic susceptibility of CuO at temperatures above 100 K, i.e., far above the Curie tail region, is about 13 – 17 times of that in bulk copper and can be used as a parameter to estimate the content of CuO in Cu nanocrystals. With the values of χ (200 K) in Table II, the content of CuO in Cu nanocrystals is estimated to be about 4 ~ 8%. Although the determination of real value of magnetic susceptibility is difficult owing to its strong sample dependence, the result is still approximately close to the values 3 – 5% estimated by specific heats above.

TABLE II. The magnetic susceptibility of CuO, bulk copper, 500 Å Cu nanocrystals and its counterparts at 50 °C and 200 °C and associated parameters derived from data below 20 K.

Sample	χ (200 K) (emu/mol Cu)	c (emu K/mol Cu)	θ (K)
500 Å Copper Nanocrystals	1.7×10^{-5}	4.38×10^{-4}	13.8
50 °C Hz-annealing Cu nanocrystals	1.5×10^{-5}	3.52×10^{-4}	13.3
200 °C Hz-annealing Cu nanocrystals	-0.25×10^{-5}	1.25×10^{-4}	1.6
Bulk copper	-0.7×10^{-5}	5.83×10^{-6}	2.47
Copper oxide	9.0×10^{-5}	2.06×10^{-4}	0.82

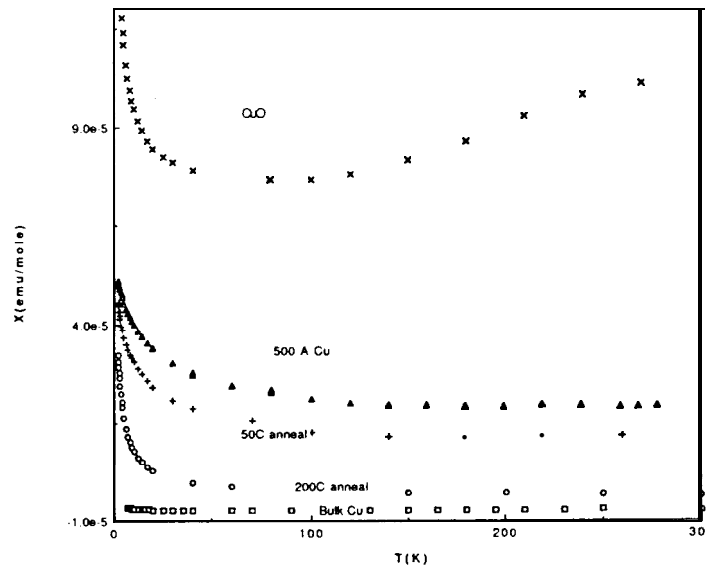


FIG. 2. Temperature dependence of molar magnetic susceptibility of CuO, 50 °C Hz-annealed nanocrystals, 200 °C Hz-annealed Cu nanocrystals and bulk copper.

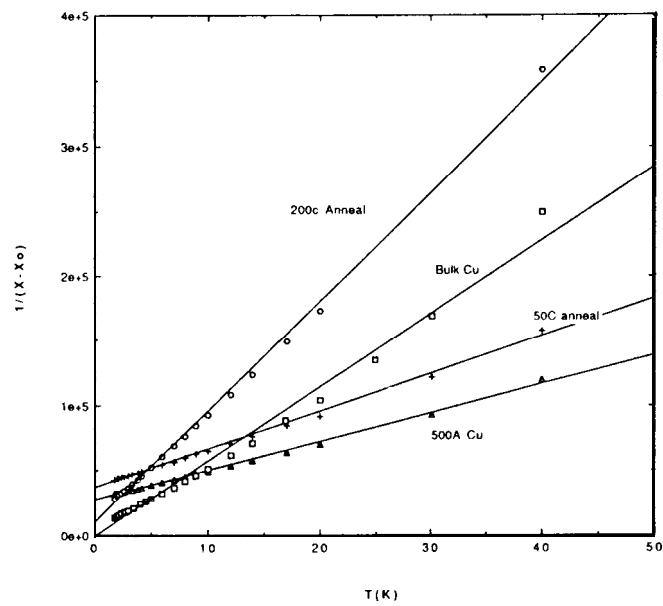


FIG. 3. Linear fits of inverse magnetic susceptibility vs. temperature for various specimens, Cu nanocrystals, 50 °C Hz-annealed Cu nanocrystals, 200 °C Hz-annealed Cu nanocrystals and bulk copper. Constant χ_0 is chosen from high temperature region data.

The theoretical calculation of magnetic susceptibility for two dimensional electrons [5] is described by

$$\chi_{el-2d} = \frac{L^2 m_e \mu_B^2}{\pi \hbar^2}, \quad (8)$$

in which m_e is the surface effective mass of electron and μ_B is Bohr magnetron. The two-dimensional magnetic susceptibility from surfaces of Pd nanocrystals is independent of temperature and it is estimated to be 7×10^{-7} emu/mol for Cu nanocrystals, by placing the calculated surfaces area 8×10^{11} cm² into Eq. (8). The value is too small as compared with the difference of susceptibility between 50 °C Hz-annealed and 200 °C Hz-annealed samples, due to crystal growth and surface reduction at 200 °C annealing. This manifests that most change in magnetic susceptibility between the two temperature annealed specimens is not totally originated from the surface of Cu nanocrystals and might be from inter-grain boundaries, disorders, defects and the interior Cu oxidation, the same conclusion as derived above from specific heat.

To examine the effect of surface stress on the variation of lattice parameters, the X-ray spectra for Cu nanocrystals and bulk copper were taken, the lattice constants are 3.6276 Å and 3.6299 Å for Cu nanocrystals and bulk copper, respectively. Whether this slight decrease of -0.06% in Cu nanocrystals is related to the outcomes discussed above needs further study.

IV. CONCLUSIONS

We have seen the two dimensional characteristics in 500 Å Cu nanocrystals through the measurements of low temperature specific heat and magnetic susceptibility. Hz-annealing at 50 °C which is below the crystal growth temperature, makes no big effect on the properties of Cu nanocrystals. While 200 °C Ha-annealing has transformed Cu nanocrystals to bulk-like form, the surface reduction can be accurately calculated from the decrease of specific heat of two dimensional phonons. The result of three-dimensional phonon specific heat indicates the possible existence of about 2 ~ 5% CuO in the interior of Cu nanocrystals. Concerning the two-dimensional electrons, the 200 °C Hi-thermal annealing reduces not only the surface electrons but also the two-dimensional electrons inside nanocrystals such as in inter-grain boundaries, defects and disorders. Since a large portion of two dimensional quantities of C(T) and X(T) still reside in bulk-like 200 °C Hz-annealed Cu nanocrystals, a large amount of intergrain boundaries, defects and disorders must be created in Cu nanocrystals at the time of their fabrication. This explains why the reported experimental data of C(T) are always much larger than the theoretical predictions [7].

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