



SPECIFIC HEAT OF FINE COPPER PARTICLES

Y. Y. Chen¹, Y.D. Yao^{1,2}, B.T. Lin¹
C. T. Suo¹, S. G. Shyu³, and H. M. Lin⁴

1 Institute of Physics, Academia Sinica, Taipei, Taiwan ROC.

2 Department of Physics, Chung Cheng Univ., Chiayi, Taiwan ROC.

3 Institute of Chemistry, Academia Sinica, Taipei, Taiwan ROC.

4 Department of Materials Engineering, Tatung Institute of
Technology, Taipei, Taiwan ROC.

Abstract - The specific heats of bulk Cu, CuO powder, and fine Cu particles with average particle sizes around 500 Å were investigated for temperatures between 1 and 20 K, and 300 and 800 K. For temperatures below roughly 20 K, a quadratic temperature term of specific heat bT^2 was observed in fine Cu particles, but not in bulk Cu and CuO powder. This is due to the contribution of the two-dimensional surface characteristics of phonons. For temperatures above 300 K, a large exothermal peak was observed for fine Cu particles near 505 K. This is due to the recombination of fine Cu particles to bulk Cu.

INTRODUCTION

In recent years, fine metal particles or nanocrystalline metals have been paid considerable attention in experimental and theoretical work (1-4). These materials are interesting from both the point of view of fundamental research for studying the interface characteristics etc, and the point of view of application for various industries, e.g. catalyzers and magnetic recording media etc. In nanocrystalline materials, a large fraction of the atoms are surface or interface atoms. Thus, any structure sensitive physical properties are expected to differ between fine particles and bulk materials. For example, the thermodynamical properties are directly related to the atomic structure; the measurement of the specific heat as a function of temperature of nanocrystalline materials should reveal differences with respect to the bulk materials (5,6). Up to now, even a variety of properties of nanocrystalline materials have been extensively studied; comparatively very little effort has been devoted to the specific heat study of fine particles.

In this investigation, we report the specific heat study performed at low temperatures and the calorimetric behavior at high temperatures for fine Cu particles as well as the comparison of these differences in behavior between bulk Cu, CuO powder, and fine Cu particles.

EXPERIMENTAL

Specimens for this study were prepared from commercially available high purity Cu bulk (99.9999%), CuO (99.99%) and Cu fine powders with average particle sizes around 500 Å, bought from Vacuum Metallurgical Co., Japan. The low temperature specific heat measurements were performed with a thermal-relaxation micro-calorimeter, with specimen dimensions $2 \times 2 \times 0.8 \text{ mm}^3$. One side of the specimen was in good thermal contact with the specimen holder of micro-calorimeter. The specimen holder was semi-adiabatically isolated from the bath by four gold-copper alloy wires for thermal relaxation operation and electrical connections. For temperatures above 300 K, the calorimetric studies were performed by means of a Perkin-Elmer differential scanning calorimeter, DSC-4. The specific heat obtained in this work by DSC is not a purely specific heat, but reflects mainly the endothermic or exothermic effects. All DSC measurements were made under flowing N_2 with a heating rate of 10 K/Minute.

RESULTS AND DISCUSSION

Figure 1 shows the specific heat of bulk Cu, CuO powder, and Cu fine particles, with average particle sizes around 500 Å, as a function of temperature between 1 and 20 K. Generally speaking, the specific heat of all nonmagnetic bulk metals at low temperatures should consist of the electronic and phononic terms, which are proportional to T and T^3 , respectively. The experimental data in Figure 1 were least-square fitted to the polynomial $C(T) = aT^1 + bT^2 + cT^3$. The coefficients of the polynomial (a , b , & c) are listed in Table I. It is noticed that quite large coefficients of the quadratic term appear in fine Cu particles. They are relatively small for bulk Cu and can be treated as an experimental error. There are no linear and quadratic terms for the CuO specimens and only the T^3 term with a relatively very large coefficient c compared with bulk and Cu fine particles. The value of c for fine Cu particles is 0.066; it is slightly larger than 0.051 for the bulk Cu. This suggests that the surface atoms of fine Cu particles are oxidized. The large coefficients of the linear and quadratic terms in the specific heat of fine Cu particles can be understood qualitatively according to the theoretical analysis of two-dimensional

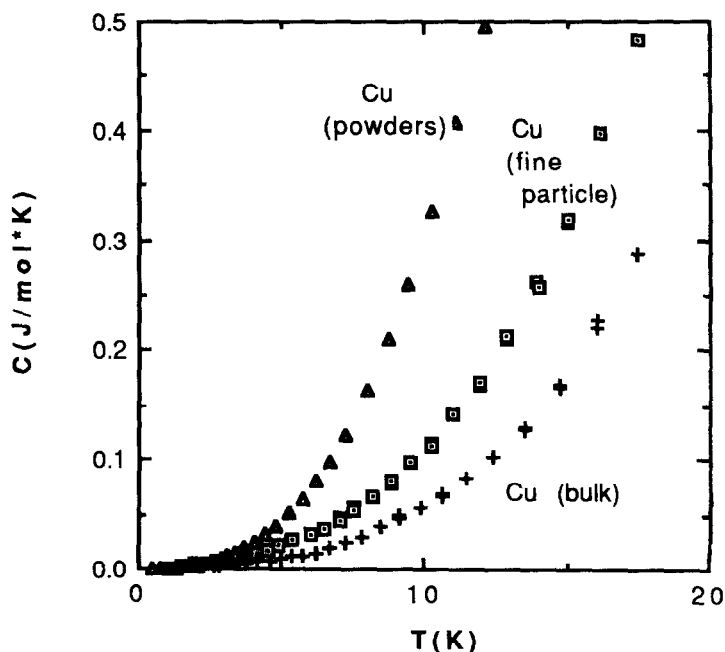


Figure 1. The specific heat of bulk Cu (+), fine Cu particle (□), and CuO powder (Δ) between 1 and 20 K.

specific heat by Chu (7). Following this theoretical analysis, the specific heat of a two-dimensional electron system is still a linear function of temperature; however, the specific heat of a two-dimensional phonon system is in a quadratic function of temperature.

TABLE 1

The Temperature Coefficients of the Specific Heat of All Specimens in the Polynomial $C(T) = aT^1 + bT^2 + cT^3$

Specimens	a (mJ/K ² mol Cu)	b (mJ/K ³ mol Cu)	c (mJ/K ⁴ mol Cu)
Cu Bulk	0.68	0.01	0.051
Cu Fine particles	1.03	0.32	0.066
CuO Powders	0.00	0.00	0.41

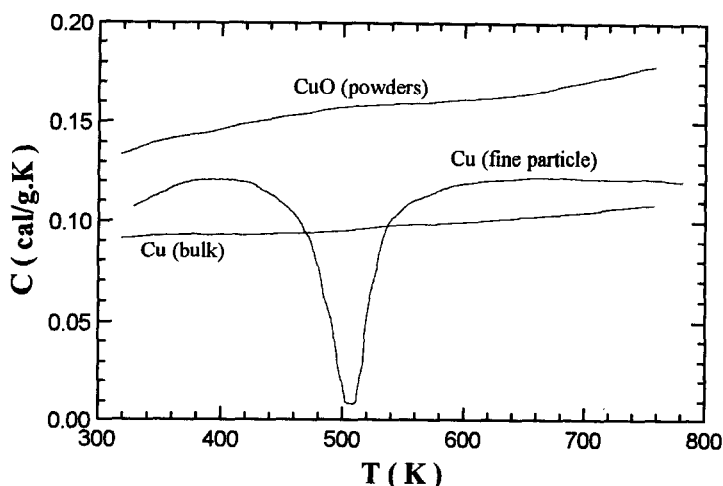


Figure 2. The specific heat of bulk Cu, fine Cu particle, and CuO as a function of T between 300 & 800 K.

Figure 2 presents the specific heat of bulk Cu, CuO powder, and fine Cu particles as a function of temperatures between 300 and 800 K. It is clear that the specific heat of fine Cu particles is higher than that of bulk Cu for temperatures roughly below 450 K. A large exothermal peak near 505 K was observed. This is due to the recombination of fine Cu particles to bulk Cu.

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