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EVIDENCE OF MULTIPLE PHASE TRANSITIONS IN SINGLE-CRYSTALLINE CuO BY DSC HEAT CAPACITY MEASUREMENT

X. G. Zheng[1], *T. Kawae*[2], *S. Tanaka*[1], *M. Suzuki*[1] *and C. N. Xu*[3]

[1]Department of Physics, Saga University, Saga 840-8502
[2]Department of Applied Quantum Physics, Faculty of Engineering, Kyushu University Fukuoka 812-8581
[3]Kyushu National Industrial Research Institute, Tosu, 841-0052, Japan

Abstract

Heat capacity measurements were carried out on single-crystalline CuO in the temperature range 130–300 K. Sharp peaks corresponding to the antiferromagnetic transitions were clearly observed at 211 and 227 K. At the low-temperature end, near 160 K, a wide peak in the heat capacity signal was also demonstrated. An electric anomaly was observed in the temperature range 150–160 K, which strongly suggests the possibility of a new low-temperature phase transition in CuO. This study also indicates that DSC measurement is an effective tool to detect magnetic transitions and probe subtle phase transitions in solids.

Keywords: cupric oxide, heat capacity anomaly, magnetic phase transition

Introduction

In composition, CuO and Cu_2O are the simplest of the cuprates, among which the complicated ones display high-T_c superconductivity. For this reason, the magnetic interaction in these copper oxides is of considerable interest from the aspect of a study of the high-T_c superconductivity mechanism. In contrast with the diamagnetic Cu_2O, the magnetic properties of CuO are confusing. It was first reported by Millar that two phase transitions were observed for CuO by specific heat measurement, at 215 and 230 K [1]. However, a contradictory result was reported by Hu *et al.* who claimed only one specific heat peak, at 230 K [2], and this was later verified by neutron diffraction to be an antiferromagnetic phase transition [3, 4]. Perakis *et al.* reported that the susceptibility of granular CuO did not reach a maximum until 540 K [5], whereas Okeeffe *et al.* reported that the susceptibility fell to a plateau below 150 K without any anomalous behaviour at T_N [6]. Since then, magnetic susceptibility, heat capacity and neutron diffraction measurements have been reported and many of them tend to confirm the two magnetic transitions: magnetic ordering near 230 K, followed by a first-order spin reorientation at 215 K [7–10]. Although the heat capacity measurement was the first to reveal the existence of the two transitions, the resolution of the data was not sufficiently high and convincing; especially the

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peak indicating the 215 K transition was obscure. It should be noted that, with the exception of one of the neutron diffraction studies, these measurements were made with powder or sintered samples of CuO. The sample dependency was marked, as can be seen from the neutron diffraction results on powders of CuO [3, 4], which detected only the 230 K transition, and those on crystal [10], which detected the two transitions. We have recently developed a modified chemical vapour transport method to grow single-crystals of CuO [11]. As a result, heat capacity and electric magnetic measurements on high-quality single-crystalline CuO have become available. This article reports the results of heat capacity measurements on single-crystalline CuO.

Crystals growth and experimental procedures

The single-crystal was grown by a novel chemical transport vapour growth method [11]. Powders of CuI (99.99%) and BaO_2 (99.9%) were enclosed in a quartz glass tube (∅20×150 mm) at a high vacuum of 10^{-5} Torr, then set into a two-zone electrical furnace (high-temperature zone: 900°C; growth zone 800°C) and heated for one week. The amount of CuI was weighed to give a iodine concentration of 5 mg cm^{-3} in the tube. BaO_2 was weighed according to the reaction $2CuI+2BaO_2=2CuO+2BaO+I_2$. CuO powder (99.9%) was added to the quartz tube to increase the vapour pressure. Shiny black crystals in plate form with dimensions up to 14×3×0.3 mm, and also in a square form of 5 mm^3 (Fig. 1), were grown at the low-temperature end of the quartz tube. X-ray diffraction and Laue reflection patterns proved the single-crystal nature. EDX analysis showed that the single-crystals contained no impurities of barium, iodine or other elements except copper. The XRD spectrum for the single-crystals in this study shows that the structure is monoclinic with unit cell dimensions of a=4.69 Å, b=3.42 Å, c=5.13 Å, β=99.5°, in consistency with previous reports on copper(II) oxide [12, 13].

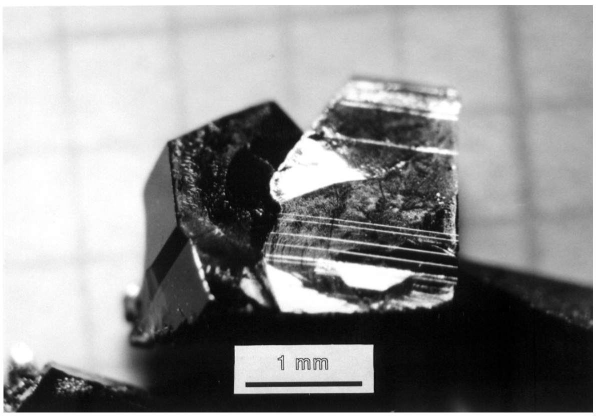

Fig. 1 Photograph of single-crystal of CuO

In order to examine the influence of possible deviations from oxygen stoichiometry, the single-crystals were heated to 400°C and annealed in flowing oxygen and argon gases. DSC measurements were made in the temperature range 130–300 K, using a Seiko DSC 120 calorimeter with a sensitivity of 0.4 μW. For each measurement, 20 mg CuO was used with α-Al_2O_3 as reference. Aluminium cells were utilized as the containers. The cooling and heating were maintained at 1 and 5 K min^{-1}, respectively. For the specific heat mode, a cooling rate of 5 K min^{-1} was used. Sapphire crystal applied as standard material for specific heat calculation.

Results and discussion

Antiferromagnetic transitions

Figure 2 depicts the specific heat results for a single-crystal of CuO. In this temperature range, no difference was observed for the single-crystals that were differently annealed, and therefore only the specific heat for the as-grown single-crystal is shown. Two peaks were clearly seen in the C_p *vs.* T data, at 211 and 227 K. The 211 K transition in the single-crystals was especially sharp. Unlike the previously reported small and poorly resolved anomaly in the specific heat, the present results clearly show the existence of two phase transitions in CuO. The neutron diffraction study revealed that the two peaks corresponded to a paramagnetic to incommensurate AF transition at T_N=230 K, and a further transition to commensurate AF order at 213 K, with spin reorientation of the antiferromagnetic ordering [9, 10]. It is seen that the reorientation is prominent in single-crystal samples. The present heat capacity data are of much higher resolution than the previously reported data based on powders or sintered CuO and clearly show the magnetic transitions. This reconfirms that heat capacity measurement is a very effective tool to probe phase transitions in single-crystals of CuO.

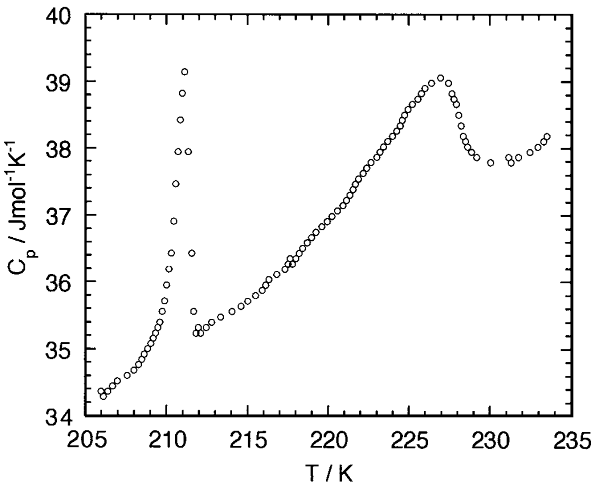

Fig. 2 Temperature-dependence of specific heat of a single-crystal of CuO corresponding to the antiferromagnetic transitions

A low-temperature transition

For the oxygen-annealed single-crystals, however, we found traces of peak-like features in the DSC signal at lower temperatures. Figure 3 illustrates the raw DSC data on an oxygen-annealed CuO crystal with α-Al_2O_3 as reference. A small peak-like feature can be recognized at around 160 K. This alone cannot be regarded as suggesting a phase transition. However, we also found anomalies in both electric and magnetic properties [14]. For the as-grown crystal, semiconductive behaviour similar to that reported previously was observed with an activation energy of 0.11 eV, which could be explained by the existence of a micro quantity of Cu^{+3}, as suggested by DeSisto *et al.* [15]. Nevertheless, a prominent shoulder feature caused by a resistivity drop at around 150–160 K is present in the curves for oxygen-annealed crystals (Fig. 4). On the other hand, the feature seen for oxygen-annealed CuO nearly vanished on further annealing of these crystals in Ar gas. In the DC magnetization measurements, a small anomaly of the susceptibility at around 160 K is recognized for oxygen-annealed CuO on plotting a differential of the susceptibility *vs.* temperature, indicating that the resistivity anomaly is accompanied by some kind of magnetic transition.

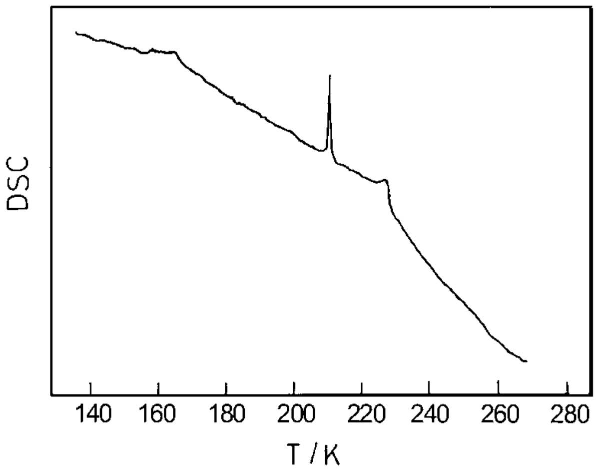

Fig. 3 DSC characteristics of an oxygen-annealed CuO single-crystal

The antiferromagnetic transition at 230 K has been reported to involve super-exchange via an intervening oxygen ion along [–1 0 1] [3, 6]. Reference to the structure of CuO shows that the nearest oxygen ions are in the [–1 0 1] plane. Since this image is determined by the crystal structure, i.e. Cu–O distances and angles, the anomaly seen in oxygen-annealed CuO is possibly caused by a small structural transformation at low temperatures, induced by hole-doping, or it may even be related to an effect of spin excitation similar to the spin gap phenomena in an underdoped high-T_c superconductor [16].

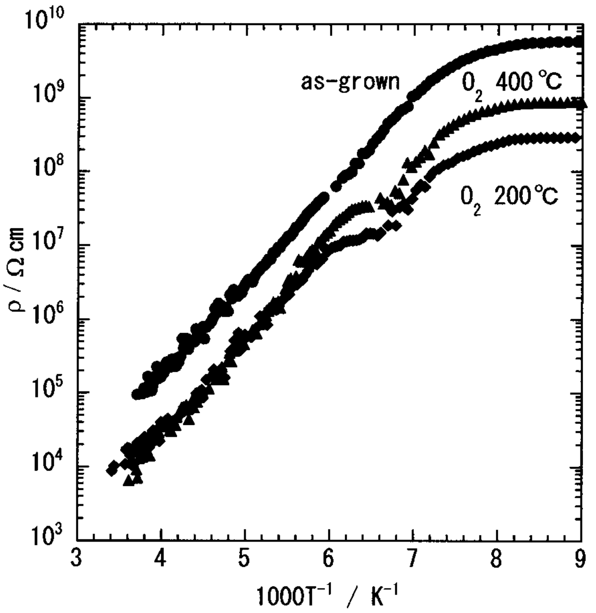

Fig. 4 Temperature-dependences of electric resistivities of as-grown and oxygen-annealed CuO crystals

Conclusions

In summary, heat capacity measurements on single-crystalline CuO clearly demonstrated the antiferromagnetic transitions at 211 and 227 K, and suggested a transition at around 160 K. This study also shows that DSC measurement is an effective tool for the detection of magnetic transitions and the probing of subtle phase transitions.

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