

Heat capacity of CuO in the temperature range of 298.15–1300 K

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Abstract

The isobaric heat capacity of CuO was measured in the temperature range of 350–1130 K by DSC. The temperature dependence of the heat capacity exhibits rather unusual course which can be explained by significant magnetic contribution extending up to ≈ 900 K. The derived heat capacity polynomial equation fits the published experimental heat content data up to 1300 K with sufficient accuracy. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Cupric oxide (CuO) has recently attracted wide attention because of its relationship to high temperature superconductors. Its thermodynamic properties have been reevaluated and new temperature dependencies of the heat capacity have been derived [1,2]. In both assessments as well as in the JANAF Tables [3], the value of C_{pm}° (298.15 K) is based on the low-temperature heat capacity measurements of Hu and Johnston [4] ($42.30 \text{ J K}^{-1} \text{ mol}^{-1}$). This value is in agreement with the older one reported by Millar [5] ($42.7 \text{ J K}^{-1} \text{ mol}^{-1}$) and it has also been confirmed by recent measurements by Gmelin et al. [6–8] ($42.18 \text{ J K}^{-1} \text{ mol}^{-1}$) and Junod et al. [9,10] ($41.80 \text{ J K}^{-1} \text{ mol}^{-1}$). Heat content measurements by Wöhler and Jochum [11] and Mah et al. [12] have been used to evaluate the temperature dependence of C_{pm}°

above room temperature in the above mentioned assessments [1,2]. Recommended values lie on a smooth, continuously increasing curve given by a simple equation

$$C_{\text{pm}}^{\circ} = a + bT + \frac{c}{T^2} \quad (1)$$

with $a, b > 0$ and $c < 0$. Tabulated JANAF data [3] also show the same course. Additional heat content measurements for the temperature of 873 K performed by Boudène et al. [1] and for 977 K by Zhou and Navrotsky [13] have confirmed the results of Mah et al. [12]. Gmelin et al. [6–8] have measured heat capacity of CuO by DSC up to 1000 K and pointed out that, in contrary to the results of heat content measurements, there is a small broad maximum on the temperature dependence between 700–900 K. Gmelin et al. explained this unusual behavior by significant magnetic heat capacity contribution up to 1000 K.

In this paper, we report the results of heat capacity measurements for polycrystalline cupric oxide in the temperature range of 350–1130 K using DSC.

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2. Experimental

Multidetector high temperature calorimeter SETARAM with heat flux DSC detector was used for the heat capacity measurements [14,15]. Step heating method with reference (synthetic sapphire, NIST standard reference material No. 720) was applied. Totally 40 steps consisting of 5000 s isothermal delay followed by 20 K temperature step with heating rate of 1 K min⁻¹ covered the temperature range of 350–1130 K. All measurements were performed in air. Three experimental runs with powdered CuO (Aldrich, 99.99 wt.%) samples of masses about 1.7 g were carried out. The samples as well as the reference specimen were preheated up to 1130 K before each measurement.

The accuracy of the present measurement was checked by measuring the heat capacity of a standard α -Al₂O₃ sample. Relative error of the observed values against the corresponding values of NIST certificate was found to be less than $\pm 2\%$.

3. Results and discussion

The experimental values of the heat capacity are shown in Fig. 1. The experimental data were fitted to various polynomials as a function of temperature by

weighted least squares method using the boundary condition $C_{\text{pm}}^{\circ}(298.15 \text{ K})=42.2 \text{ J K}^{-1} \text{ mol}^{-1}$. Our analysis indicates that the equation

$$C_{\text{pm}}^{\circ} = 37.50 + 14.43 \times 10^{-3} T + \frac{3.448 \times 10^6}{T^2} - \frac{1.017 \times 10^9}{T^3} \quad (2)$$

fits the experimental data satisfactorily well (the mean square deviation $\sigma=1.43$, average relative deviation is 2.1%). This dependence has no extremes in the studied temperature range, however, there is an inflex point at $T=590 \text{ K}$. The extrapolation to the temperature 1300 K gives the value $C_{\text{pm}}^{\circ}(1300 \text{ K})=57.83 \text{ J K}^{-1} \text{ mol}^{-1}$ which is essentially the same as $57.80 \text{ J K}^{-1} \text{ mol}^{-1}$ given in the JANAF Tables [3].

Contrary to the results of Gmelin et al. [6–8], the suggested temperature dependence of C_{pm}° , does not indicate any maximum. Although it is possible to obtain an equation including T^2 and T^3 terms with a maximum at 665 K and a very shallow minimum at 814 K, such a regression curve is statistically nearly undistinguishable from Eq. (2) ($\sigma=1.31$), however, the extrapolation to high temperatures yields incorrect results ($C_{\text{pm}}^{\circ}(1300 \text{ K}) 72.76 \text{ J K}^{-1} \text{ mol}^{-1}$). Nevertheless, the unusual shape of our curve confirms the Gmelin's conclusion about the significance of the magnetic heat capacity contribution (C_{mg}) well above Néel transition temperature $T_{\text{N}}=228.5 \text{ K}$. Using the

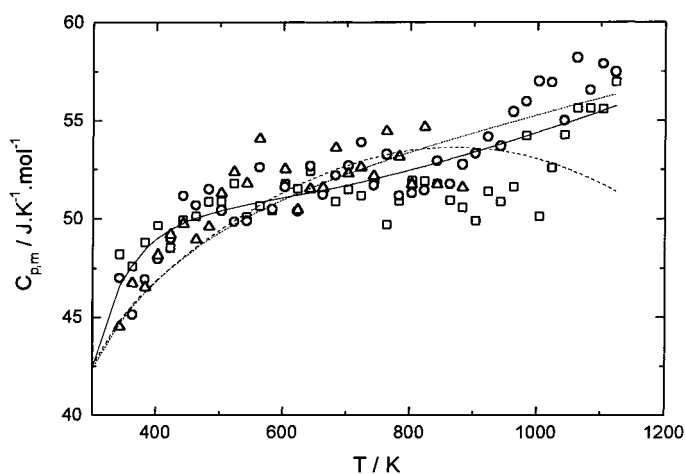


Fig. 1. Isobaric molar heat capacity of CuO as a function of temperature: (○) run 17a; (□) run 18; (△) run 20; (---) Ref. [8]; (···) Ref. [3]; (—) this work.

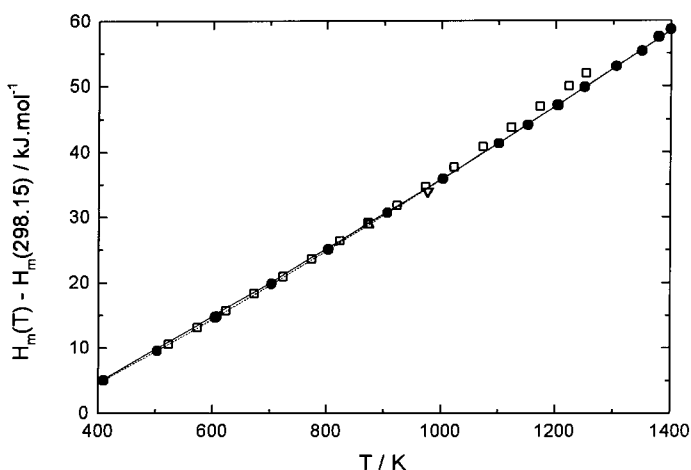


Fig. 2. Temperature dependence of heat content of CuO: (□) Ref. [11]; (●) Ref. [12]; (△) Ref. [1]; (▽) Ref. [13]; (· · ·) Ref. [3]; (—) this work.

same procedure as Gmelin [6], C_{mg} was calculated from our experimental C_{pm}^o data in the temperature interval from 298.15 to 1150 K by subtracting three contributions to the total heat capacity, namely, dilatation (C_d), Debye lattice (C_l) and electronic part (C_e). The calculated temperature dependence of C_{mg} passes through a maximum of $\approx 4 \text{ J K}^{-1} \text{ mol}^{-1}$ at the temperature of 370 K and a shallow minimum of $0.7 \text{ J K}^{-1} \text{ mol}^{-1}$ at 850 K. Furthermore, it increases up to $1.3 \text{ J K}^{-1} \text{ mol}^{-1}$ at 1150 K. A similar trend of the temperature dependence of C_{mg} (strictly speaking the temperature dependence of the difference $C_{pm}^o - C_d - C_l - C_e$) has been observed by Chuang et al. [16] for nickel and iron and has been attributed to higher order anharmonic vibrations, not completely covered by C_d [16].

Fig. 2 shows a comparison of the experimental heat content data [1,11–13] with the values derived from Eq. (2). The agreement up to 1150 K is acceptable ($\sigma=431$). Some discrepancies between the Wöhler and Jochum's data [11] and our (extrapolated) values exist at higher temperatures. The mean square deviation for optimized C_{pm}^o temperature dependencies given in [1,2] is $\sigma=389$ in both cases and for the JANAF Tables data $\sigma=405$ (only data for temperature up to 1150 K were considered).

The proposed temperature dependence of the standard molar heat capacity of CuO seems to be correct and reliable and Eq. (2) can be used in the temperature range from 298.15 K up to 1300 K.

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