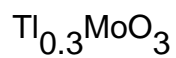


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The specific heat study of charge-density-wave phase transitions for the blue bronze $\text{Tl}_{0.3}\text{MoO}_3$

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Abstract. The specific heat of the blue bronze $\text{Tl}_{0.3}\text{MoO}_3$ is measured using an adiabatic continuous heating method from 100 to 220 K. A specific heat anomaly is observed at 172.3 K. The specific heat jump, and enthalpy and entropy changes associated with the CDW phase transition are estimated. The results suggest that the phase transition is of second order and that the lattice plays an important role in thermodynamics in this system, by analogy with the behaviour of its isostructural compound $\text{K}_{0.3}\text{MoO}_3$. The mean-field theory seems not to be adequate for describing the CDW phase transition in this compound.

The blue molybdenum oxide bronzes $\text{A}_{0.3}\text{MoO}_3$ ($\text{A} = \text{K}, \text{Rb}, \text{Tl}$) are quasi-one-dimensional conductors at room temperature and undergo a metal–semiconductor transition at around 180 K, which is known as the charge-density-wave- (CDW-) driven Peierls phase transition [1, 2]. Recently, continued interest has been focused on various aspects in these compounds [3]. Some groups reported specific heat (C_p) investigations of $\text{K}_{0.3}\text{MoO}_3$, and their results have revealed some differences [4–7]. It is of interest to compare the thermodynamic behaviour of $\text{K}_{0.3}\text{MoO}_3$ with that of its isostructural analogue $\text{Tl}_{0.3}\text{MoO}_3$. In this paper, we present our results on the specific heat C_p of single-crystalline $\text{Tl}_{0.3}\text{MoO}_3$ from 100 up to 220 K, with special emphasis on the behaviour near the phase transition temperature T_p . For comparison, we also measured C_p for $\text{K}_{0.3}\text{MoO}_3$ over the same temperature range. The results are compared with the mean-field prediction.

The single crystals were separately grown from melts of Tl_2CO_3 , K_2CO_3 and MoO_3 by the electrolytic reduction method and found to be of good quality via examination by electron probe microanalysis and four-circle single-crystal diffraction as described elsewhere [8]. The phase transition and the non-linear transport properties of samples from the same batch were observed in resistivity, thermoelectric power and Raman scattering measurements [9–11]. The largest single crystals, which had the dimensions $7 \times 3.5 \times 1.8 \text{ mm}^3$ with mass 120 mg for $\text{Tl}_{0.3}\text{MoO}_3$ and $7.5 \times 3.2 \times 1.6 \text{ mm}^3$ with mass 114 mg for $\text{K}_{0.3}\text{MoO}_3$ respectively, were used for the specific heat study. The specific heat was measured by employing the adiabatic continuous heating method first developed by Junod in 1979 [12]. The sample

together with a Pt thermometer was attached to a sapphire substrate 100 μm thick. On the opposite side of the sapphire a strain gauge was glued using GE7031 varnish, as the sample heater. The addenda, including the sapphire substrate, the thermometer, the heater and the links to the chamber, contribute less than 30% of the total specific heat over the whole temperature range. In order to make the tiny specific heat anomaly of small samples visible and suitable for analysis, considerable effort was made to reduce the heat exchange further and to realize full computer control. As a result, the relative temperature resolution $\Delta T/T$ was better than 10^{-5} , and the absolute accuracy of the specific heat is found to be less than 1% by comparing the result for standard copper with the literature [12]. The heating rate was about 1 K min^{-1} .

Figure 1 shows the temperature variation of the C_p for $\text{Ti}_{0.3}\text{MoO}_3$ and $\text{K}_{0.3}\text{MoO}_3$. The magnitude of C_p for $\text{K}_{0.3}\text{MoO}_3$ is of the same order as the value previously reported by Konate [4] and Kwok *et al* [6]. Over the chosen temperature range, the value of C_p of $\text{Ti}_{0.3}\text{MoO}_3$ is less than that of $\text{K}_{0.3}\text{MoO}_3$; this seems to imply that the Debye temperature of $\text{Ti}_{0.3}\text{MoO}_3$ is higher than that of $\text{K}_{0.3}\text{MoO}_3$. Two anomalies were found at 172.3 K and 177.5 K in $\text{Ti}_{0.3}\text{MoO}_3$ and $\text{K}_{0.3}\text{MoO}_3$ respectively, in correspondence with the CDW transition, where the anomalies of the electric resistivity, magnetic susceptibility and thermoelectric power were observed [3, 9–11].

In order to analyse the features of the specific heat, the regular contribution from the background thermal excitation must be subtracted from the total. Here, we have adopted a procedure for accomplishing the subtraction that we believe is reasonable for this case, and most of the conclusions that we draw do not depend on the details. A polynomial fit to the background (shown as the solid line in the inset of figure 1 for $\text{Ti}_{0.3}\text{MoO}_3$) was made by forcing the error to be small at temperature far from T_p . The subtraction of the fit from the measurement gives a crude estimate of the excess specific heat ΔC_p associated with the CDW formation. The results for ΔC_p versus T for the two compounds are given in figure 2 (a) and (b); the broadened λ -type specific heat jump is observed for both compounds. Moreover, the measurements of the heat capacity were also performed in cooling runs; no apparent hysteresis with temperature variation was found. These two results suggest that the phase transition is of second order. This confirms the recent measurement of Young's modulus by Bourne *et al* [13] and the prediction of Friend *et al* that generally incommensurate CDW modulations are associated with a second-order phase transition [14]. From figure 2(b), ΔC_p for $\text{K}_{0.3}\text{MoO}_3$ is found to be 1.82 J $\text{mol}^{-1} \text{K}^{-1}$ (0.20R, where R is the gas constant). The enthalpy and entropy changes associated with the phase transition can be obtained by integrating ΔC_p and $\Delta C_p/T$ over the temperature, giving the results $\Delta H = 20.8 \text{ J mol}^{-1}$ and $\Delta S = 0.12 \text{ J mol}^{-1} \text{K}^{-1}$. These data are approximately the same as those measured by Konate *et al* [4]: $\Delta C_p \sim 1.96 \text{ J mol}^{-1} \text{K}^{-1}$, $\Delta H \sim 25 \text{ J mol}^{-1}$ and $\Delta S \sim 0.15 \text{ J mol}^{-1} \text{K}^{-1}$; those given by the fit of Johnston's specific heat measurement [15] to the XY model: $\Delta C_p \sim 1.8 \text{ J mol}^{-1} \text{K}^{-1}$; and also those determined by Hauser *et al* through thermal expansion experiments [16]: $\Delta C_p \sim 1.4 \text{ J mol}^{-1} \text{K}^{-1}$. However, the values are less than those measured by Kwok *et al*, where $\Delta C_p \sim 7.8 \text{ J mol}^{-1} \text{K}^{-1}$ and $\Delta S \sim 1.5 \text{ J mol}^{-1} \text{K}^{-1}$ [6]. Firstly, we argue that the discrepancy may arise from the differences among the samples from the different laboratories, such as the variation in the impurity content. Impurities would smear the phase transition and restrict the divergences that are expected from fluctuations. Many investigations of macroscopic properties have revealed substantial differences between compounds as regards the importance of fluctuations to phase transitions [17]. Up to now, as far as we know, the effect of fluctuations on various physical properties, and how they are related, is not well established. Secondly, we suggest that the discrepancy between our values and Kwok's values could result from the effects of the broadening

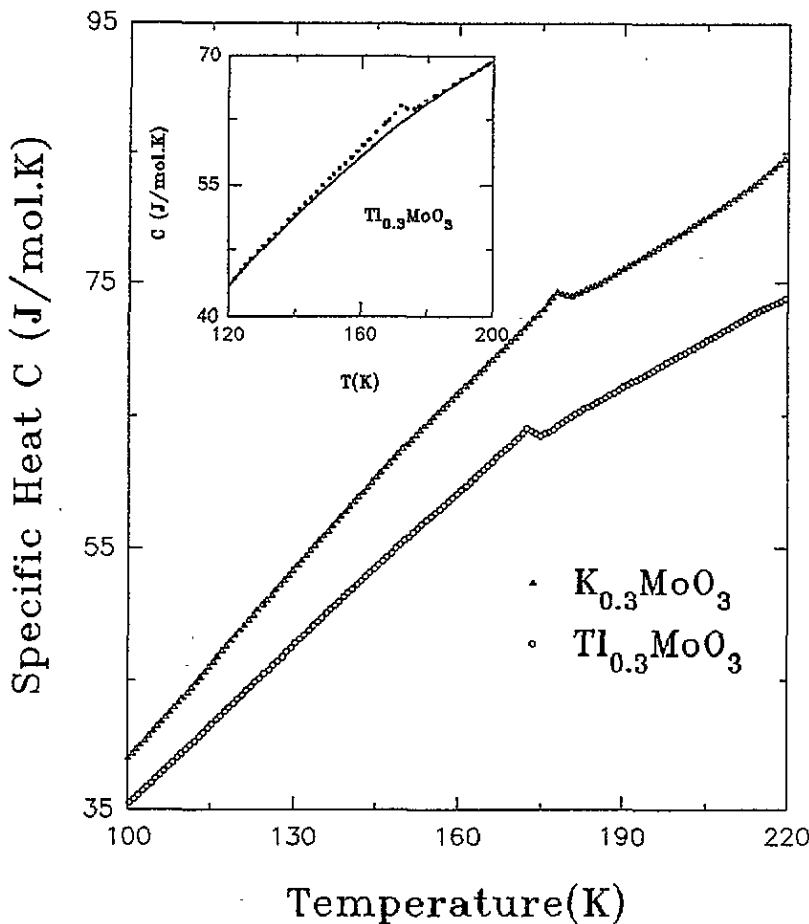


Figure 1. The temperature dependence of C_p for $Tl_{0.30}MoO_3$ and $K_{0.30}MoO_3$. Inset: the regular background specific heat of $Tl_{0.3}MoO_3$ is shown as the solid line.

of the phase transition in our crystals. A likely reason is that, in making the polynomial fit, the region where ΔC_p was set to zero, although apparently far from T_p , was actually in the wings of the broad anomaly. Because of this, the measured ΔC_p , ΔH , ΔS may be regarded as lower limits. From figure 2(a), ΔC_p , ΔH and ΔS for $Tl_{0.3}MoO_3$ are respectively $1.88 J mol^{-1} K^{-1}$ ($0.23R$), $37.0 J mol^{-1}$ and $0.23 J mol^{-1} K^{-1}$; these values are comparable to the corresponding values for $K_{0.3}MoO_3$ measured by us.

By analogy with the analysis by Kwok *et al*, we estimate the expected electronic contribution ΔC_p^e . According to mean-field theory, it is equal to $1.43\gamma T_p$, where γ is the standard electronic specific coefficient ($\pi^3/3$) $k_B^2 D(\epsilon_F)$. For $Tl_{0.3}MoO_3$, taking $D(\epsilon_F) \sim 1.89$ states $eV^{-1}/molecule$ [10], $\Delta C_p^e = 0.8 J mol^{-1} K^{-1}$. This is smaller than the value measured by us. This discrepancy can be understood qualitatively by including some contribution from the lattice, as suggested by McMillan [18]. This implies that it is possible that the description of the mean-field theory around the Peierls transition is not adequate, which is further confirmed by comparing the width of the critical region near T_p (ΔT_c). In mean-field theory ΔT_c is $\xi_T T_p$, where ξ_T is related to the Landau correlation length ξ_0 via $\xi_T = [(2\pi\xi_0)^3 \Delta C_p^e / k_B]^{-2}$ [19]. At zero temperature, $\xi_0 \sim v_F / 2\Delta(0)$, where

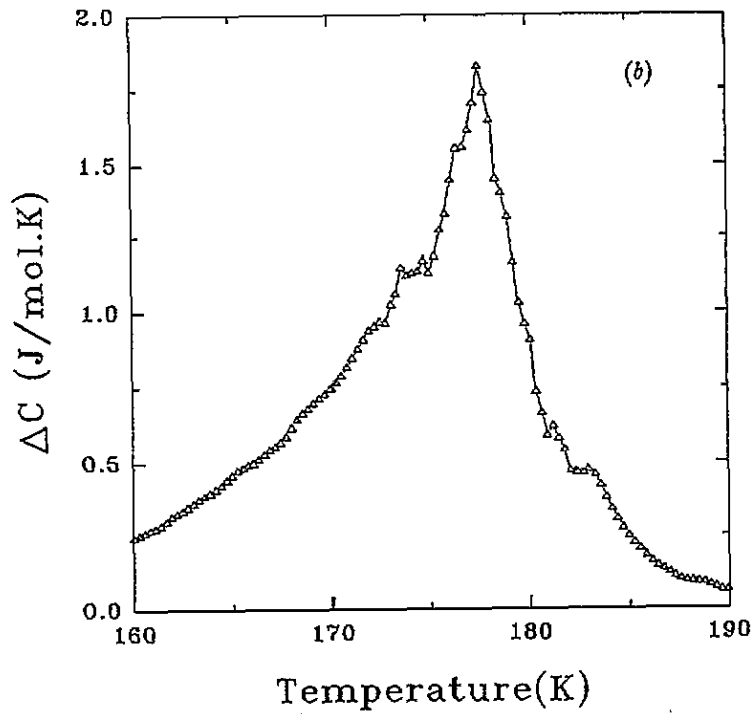
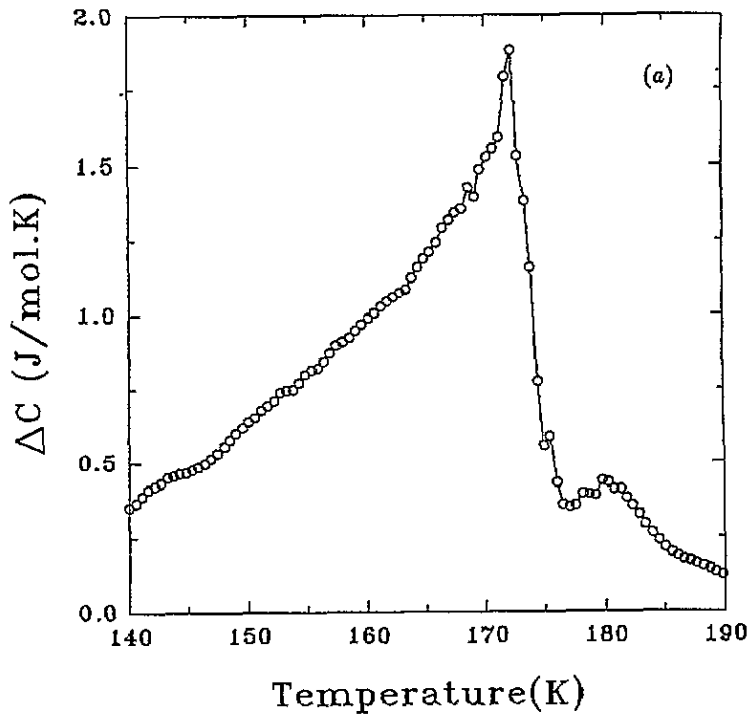


Figure 2. A plot of ΔC_p versus T . (a) $Tl_{0.30}MoO_3$ (b) $K_{0.30}MoO_3$. The solid curve is drawn to connect the experimental points.

$2\Delta(0)$ is the energy gap and $v_F \sim 2\varepsilon_F/k_F$ is the Fermi velocity. From our previously obtained data [10–11], $\varepsilon_F \simeq 0.79 \text{ eV}$, $k_F \simeq 0.3 \text{ \AA}^{-1}$, $2\Delta(0) \simeq 0.13 \text{ eV}$, for $Tl_{0.3}MoO_3$, we get $\xi_0 \simeq 39 \text{ \AA}$. Substituting in ξ_0 and ΔC_p^e values gives $\xi_T T_P \sim 0.1 \text{ K}$. However, in our measurement, the temperature region of the specific heat anomaly is above 20 K, being significantly larger than predicated by the mean-field theory. The origin of this may be that the mean-field theory neglects the effect of fluctuation of quasi-one-dimensional systems. In addition to the effect of fluctuation, the broadening of the phase transition may be the result of macroscopic variations in T_P , caused by impurities and other crystal defects.

In conclusion, we have investigated the specific heat of CDW in blue bronze $Tl_{0.3}MoO_3$ around the Peierls transition temperature T_P . A broad and large specific heat anomaly is observed and the specific heat jump, and the enthalpy and entropy changes associated with the CDW phase transition are estimated, and are found to contrast with the mean-field prediction. The enhancement may be a result of a large contribution from the lattice.

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