Thermodynamic anomalies at the Peierls transition in blue bronze

M. Chunga, Y.-K. Kuoa, X. Zhaia, E. Figuerosa, J.W. Brilla, and G. Mozurkewicha

a)Department of Physics and Astronomy, University of Kentucky, Lexington, KY 40506-0055, U.S.A.

b)Research Laboratory, Ford Motor Company, Maildrop 3028, Dearborn, MI 48121-2053, U.S.A.

ABSTRACT: Thermodynamic response functions have been measured on pieces of a single crystal of blue bronze at its 180K charge-density-wave (CDW) transition and are analyzed using a free energy appropriate for a 3D-XY model.

Charge-density-wave (CDW) transitions in quasi-one dimensional metals have been of great interest for more than two decades [1]. Originally, most interest was in one-dimensional effects, for example, suppression of the phase transition and formation of a pseudogap [2]. Recently, there is an increase in interest in the actual (3D) phase transition [3], but there have been relatively few measurements of thermodynamic quantities of sufficient precision to compare with theory, mainly because most crystals are very small and/or too brittle (e.g., organic materials), and impurity effects are large; properties can therefore be sample dependent [4].

In this paper, we report on measurements of the specific heat and Young's moduli of the quasi-one dimensional metal blue bronze (K0.3MoO3) near its 180K CDW transition [5]. All properties are measured on pieces of the same crystal for which the thermal expansivity was previously measured [6]; blue bronze crystals have the advantage of being "large" and "cleavable", so that several experiments on the same sample are possible. Furthermore, all quantities are fit to the same free energy expression, with remarkably similar fitting parameters [5], allowing us to apply the Ehrenfest/Testardi relations [7].

Measurements of specific heat and Young's moduli were made on pieces cleaved from a large crystal, ≈4 mm², (sample A from Reference 6) using scotch tape method. The specific heat, shown in Figure 1, of a 2×2×0.05 mm³ piece of the crystal was measured using ac calorimetry [8]. The results are similar to those previously reported for other crystals [9], as compared in Figure 1. The Young's moduli were measured on needle-shaped crystals (typically 0.6×0.2×0.01 mm³) using a vibrating reed technique [10]. Shown in Figure 2 are the Young's moduli along the chain direction, [010], the high conductivity direction in the monoclinic unit cell, and along the sheet direction, [102], transverse to the chains [11]. The results for these crystals are similar to those previously obtained [12].

Our data are analyzed using the crossover formulation developed by Chen, Albright, and Sengers (CAS) [13]. Using the CAS free energy, ∆A, which smoothly interpolates between regular behavior far from Tc and critical behavior near Tc, the specific heat is given by [5]

\[ \Delta c_p = -T^2 \Delta A/dT^2. \] (1)

For the Young's moduli, assuming that the singular free energy only depends on stress, σ1, through its dependence on Tc [5], one deduces

\[ \frac{Y_I}{Y_0} = Y_0 \frac{\partial^2 \Delta A/\partial \sigma_1^2}{\partial^2 \Delta A/\partial \sigma_1^2} \frac{d^2 \Delta A/dT^2}{d^2 \Delta A/dT^2} - \frac{Y_0 d^2 T_c/d\sigma_1^2}{d^2 \Delta A/dT^2} d\Delta A/dT. \] (2)

The resulting fits allow us to extract the important parameters (i.e., the magnitudes of the anomalies) at the phase transition in a systematic way that does not require guessing of background variation [5].

Shown in Figures 1 and 2 are fits of Δc_p and ΔY/Y_0 to Eqns. (1) and (2), respectively, appropriate for the XY model in three dimensions [14]. In each case, a third order polynomial in T was added to the singular contribution as a background [5]. For the Young's modulus fit, we dropped the second term in Equation (2) since the measured pressure dependence indicates [dT_c/dp] > 100 kbar [d^2 T_c/dp^2] [15].

Figure 1. Specific heats of blue bronze crystals. Data for sample #A, vertically offset by 0.2R, are from Reference 9 (crystal #3 of Figure 1). Open circles: measured data; solid curves: CAS 3D-XY fit; dashed curves: background of fit and mean-field-like contribution.
From the parameters of the fits, we obtain the mean-field-like step in specific heat, \( \Delta c_{\text{step}} = 0.16R \) [5], where \( R = 8.31 \text{J/mole-K} \), which is about 3 times larger than that estimated from BCS-type mean-field theory, assuming the electronic specific heat coefficient from Reference [16] and the suppression of the transition temperature by 3D fluctuations from its mean-field value by \( \Delta T_c \approx 16 \text{K} \), which agrees with x-ray investigations [14].

Comparisons of \( \Delta c_{\text{step}} \) and the thermal expansion coefficients \( (\Delta \alpha_{[010]} \) and \( \Delta \alpha_{[102]} \)) from Reference [6], fit to the same free energy [5,6], by the Ehrenfest/Testardi relations [7], give \( dT_c/\alpha_{[010]} = -0.65 \text{K/kbar} \) and \( dT_c/\alpha_{[102]} = -2.2 \text{K/kbar} \). If we assume that \( dT_c/\alpha_{[010]} = 0 \) (because \( \Delta \alpha_{[010]} = 0 \)) [6], then the pressure dependence of transition temperature \( dT_c/dP = \frac{-dT_c/\alpha_{[010]} + dT_c/\alpha_{[102]} + dT_c/\alpha_{[201]}}{3} = -1.5 \text{K/kbar} \), very close to the measured value of -1.4 K/kbar [15]. Comparisons with the Young's moduli anomalies then give \( Y_{[010]} = 203 \text{GPa} \) and \( Y_{[102]} = 250 \text{GPa} \).

The fit also enables us to find the critical piece of specific heat by subtracting the background and mean-field-like piece from the measured specific heat. Shown in Figure 3 is the log-log plot near the transition temperature, where \( T_c \) is chosen from the fit [5,9]. As shown in the Figure, we estimate the temperature region \( (\Delta T_G) \), where the fluctuations are approximately Gaussian, to be about 12 K. From the Ginzburg criteria, the coherence length \( (\xi_0) \) of 4.4Å can be estimated, comparable to the published value [14]. However, we note that due to the sixth power of \( \xi_0 \) in the Ginzburg criteria, \( \xi_0 \) is very insensitive to the choice of \( \Delta T_G \).

In conclusion, we have presented the results of measurements of the specific heat and Young's modulus along [010] and [102] directions on the same crystal of blue bronze for which the thermal expansion coefficient had previously measured. All quantities are fit to the free energy expression developed by Chen, Albright, and Sengers, appropriate for the 3D-XY model. From the fit, important thermodynamic parameters, suitable for comparison to microscopic models are obtained.

We would like to thank C.P. Brock for assistance in X-ray diffraction and R.H. McKenzie for helpful discussions. This research was supported in part by the National Science Foundation, Grants # DMR-9300507 and EHR-9108764.

References:
1. For a review, see G. Gruner, Rev. Mod. Phys. 60 (1989) 1129.
7. P. Ehrenfest, Leiden Comm. Suppl. 75b (1933) 8;