Thermodynamics of the Charge-Density-Wave Transition in Blue Bronze

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(Received 6 June 1994)

Specific heat, Young’s moduli, and magnetic susceptibility have been measured on pieces of a single crystal of blue bronze (for which thermal expansivity was previously measured) at its 180 K charge-density-wave (CDW) transition. All quantities were analyzed using a free energy appropriate for a three-dimensional XY model. Although not all parameters can be readily interpreted, the resulting fits permit quantification of the magnitudes of the anomalies at the phase transition in a systematic way that does not require guessing of the background variation.

PACS numbers: 71.45.Lt, 62.65.+k, 65.40.Hq, 64.60.Fr

Quasi-one-dimensional metals are of interest because of the large variety of phase transitions they exhibit, most commonly charge-density-wave (CDW) transitions [1]. A large number of measurements of thermodynamic changes at CDW phase transitions in quasi-one-dimensional metals have been made [2–9]. Although one-dimensional fluctuations are large and can be observed at temperatures much above the transitions [7,10], the phase transitions mark the onset of three-dimensional coherence of the order parameter [11]. CDW phase transitions in quasi-one-dimensional metals are expected to belong to the “3D XY” criticality class, where the two components of the three-dimensional order parameter can be taken as the amplitude and phase of the CDW [1,10]. For ideal samples, the specific heat would exhibit a very sharp cusp ($\sim 1 - [T/T_c - 1]^{0.007}$) [12]; in practice, defects wipe out the critical cusp [8], leaving the milder correction to scaling cusp [13] and mean-field-like step.

Workers have attempted to compare discontinuities in thermodynamic response functions, such as specific heat and elastic constants [2–6], using the Ehrenfest relations for mean-field transitions [14], as modified for anisotropic materials by Testardi [15,16]. Such comparisons are complicated by the facts that (i) the anomalies can be very sample dependent; (ii) the transitions are not very “mean-field-like,” the critical regions are relatively broad, and corrections to scaling behavior are non-negligible, making it necessary to apply analysis over wide temperature intervals; but (iii) the transition temperatures are typically appreciable fractions of the Debye temperature, so that the background variations of the response functions are nontrivial and poorly known.

In this Letter, we report on measurements of the specific heat, Young’s moduli (in three crystallographic directions), and magnetic susceptibility of the quasi-one-dimensional metal blue bronze ($\text{K}_{0.3}\text{MoO}_3$) near its 180 K CDW transition [17]. All properties are measured on pieces of the same single crystal for which the thermal expansivity had previously been measured [6]. Furthermore, all quantities are fit as derivatives of the same free energy expression, with remarkably similar fitting parameters, allowing the backgrounds to be consistently extracted and the discontinuities and temperature dependences of different properties to be unambiguously compared. This work constitutes, by far, the most comprehensive set of thermodynamic measurements and the most thorough test of the Testardi and Ehrenfest relations for a quasi-one-dimensional metal. While one parameter of the fitting function may be unphysically large, as discussed below, the self-consistency of the results indicates the possibility of determining several quantities precisely enough to test microscopic models of the phase transition.

The basic structural units of blue bronze are $\text{MoO}_6$ octahedra which form edge-sharing clusters arranged in chains which run along [010], the high conductivity direction in the monoclinic unit cell [18]. The chains are in turn bonded in sheets, parallel to [102] which are separated by potassium ions [18], so that crystals are easily cleaved along (201). A large crystal, $\approx 4 \text{ mm}^3$ (sample A from Ref. [6]), was cleaved using sticky tape into small pieces for measurements of specific heat and Young’s moduli. In addition, approximately 20 mg of powder obtained from this crystal was used to measure the magnetic susceptibility, using a Faraday balance. We note that the parent crystal was noticeably inhomogeneous; the dark blue color of the $\text{K}_{0.3}\text{MoO}_3$ was marbled with a white material, which should have no effect on anomalous properties at T_c.

The specific heat, shown in Fig. 1(a), of a $2 \times 2 \times 0.05 \text{ mm}^3$ piece of the crystal was measured using ac calorimetry [19]. The results are similar to those previously reported for other crystals [9]; however, Kwok, Gruner, and Brown reported a much larger anomaly [8]. Also shown is the thermal expansion coefficient along [102] of the parent crystal [6].

The Young’s moduli were measured on three cleaved needles ($\approx 0.6 \times 0.2 \times 0.01 \text{ mm}^3$) using a vibrating reed technique [20]. The fundamental flexural resonant
\[ \lambda \text{ gives the ultraviolet cutoff; the maximum fluctuation wave vector is } q_{\text{max}} = \frac{\lambda}{\xi_0}, \text{ where } \xi_0 \text{ is the mean-field coherence length [23].} \]

The singular part of the specific heat is given by
\[ \Delta c_p = \frac{T}{d} \frac{dS}{dT} = -\left[TA_{00}\right]d^2g/dT^2, \quad (2) \]

Where \( S \) is the entropy density. To find the anomalies in thermal expansion coefficients and elastic compliances, \( \Delta A \) must also be expressed as a function of the stress components, \( \sigma_i \). Making the simplifying assumption that \( A_{00}, \bar{u}, \text{ and } \lambda \) are independent of stress [5,6], so that
\[ d\Delta A/d\sigma_i = (\partial\Delta A/\partial T_c) dT_c/d\sigma_i, \quad (3) \]

then
\[ \Delta\sigma_i = -\frac{\partial^2\Delta A/\partial T}{\partial \sigma_i} \approx [A_0 dT_c/d\sigma_i] d^2g/dT^2 \quad (4a) \]

\[ = -(\Delta c_p/T) dT_c/d\sigma_i \quad (4a) \]

and
\[ \Delta Y_i/Y_{0i} \approx -Y_{0i}\Delta s_{ii} = Y_{0i}\Delta A/\Delta \sigma_i^2 \]

\[ \approx [A_0 Y_{0i}(dT_c/d\sigma_i)]^2 d^2g/dT^2 \]

\[ - [A_0 Y_{0i} d^2T_c/d\sigma_i] d g/dT \quad (5) \]

\[ = -(Y_{0i}\Delta c_p/T)(dT_c/d\sigma_i)^2 + Y_{0i} \Delta S d^2T_c/d\sigma_i^2. \quad (5a) \]

Equations (4a) and (5a) are the Ehrenfest relations [14], as generalized by Testardi for anisotropic materials [15] and general phase transitions [16] [with the assumption of Eq. (3)].

Shown in Fig. 1 are fits of \( \Delta c_p \) and \( \Delta\sigma_{[02]} \) by Eqs. (2) and (4), respectively, using the CAS free energy in the 3D XY model [10]. In each case, the fitting parameters are \( T_c, \bar{u}, \lambda, \text{ and the magnitude of the anomaly (factors in square brackets); cubic polynomials in } T \text{ were added as backgrounds, so the fits (about 200 points each) have 8 parameters. To include the effects of defect broadening, the CAS function was smoothed by } \pm 0.6 \text{ K. The parameters of the fits, which do not depend significantly (} \Delta \bar{u} < 1% \text{ and } \Delta \lambda < 6% \text{) on the order of the polynomial used or amount of smoothing, are listed in Table I. (The parameters for } \alpha_{[02]} \text{ differ slightly from those previously reported [6] due to improvements in the fitting program.)} \]

For the Young’s moduli, inclusion of both terms in Eq. (5) allowed too much freedom in the fit; i.e., the relative sizes of the terms proportional to the specific heat and entropy could be varied without significantly affecting the goodness of fit. The observed pressure dependence is, in fact, quite linear [24]: \[ dT_c/d\rho = -1.4 \text{ K/kbar while } d^2T_c/d\rho^2 < 0.01 \text{ K/kbar}^2. \] We therefore assumed the entropy term in Eq. (5) was zero; the resulting fits are shown in Fig. 1(b), with parameters listed in Table I.

The temperature derivatives of the singular free energy \( g \) for the extreme cases (\( \bar{u} = 2.55, \lambda = 0.66 \text{ and } \bar{u} = 2.46, \lambda = 0.55 \)) are shown in Fig. 2. The small variation of critical parameters obtained for the five fits indicates that
TABLE I. Fitting parameters for the CAS 3D XY fits of different response functions. For all quantities, \( T_c = 180.4 \pm 0.4 \) K, where the variation presumably results from the different thermometers used. (\( R = 8.31 \text{~J/mole~K}; \rho = 2.76 \times 10^4 \text{~mole/m}^3\)).

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Direction</th>
<th>Magnitude</th>
<th>( \bar{u} )</th>
<th>( \lambda )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta c_p )</td>
<td>---</td>
<td>( A_0/\rho )</td>
<td>0.035</td>
<td>2.56</td>
</tr>
<tr>
<td>( \Delta \alpha )</td>
<td>[102]</td>
<td>( A_0/T_c d_{T_c}/d\sigma )</td>
<td>( 1.7 \times 10^{-4} )</td>
<td>2.46</td>
</tr>
<tr>
<td>( \Delta Y/Y_0 )</td>
<td>[102]</td>
<td>( (A_0/2T_c^2) (d_{T_c}/d\sigma) R )</td>
<td>( 5.2 \times 10^{-3} )</td>
<td>2.55</td>
</tr>
<tr>
<td>( \Delta Y/Y_0 )</td>
<td>[100]</td>
<td>( (A_0/2T_c^2) (d_{T_c}/d\sigma) )</td>
<td>( 4.6 \times 10^{-3} )</td>
<td>2.55</td>
</tr>
<tr>
<td>( \Delta Y/Y_0 )</td>
<td>[010]</td>
<td>( (A_0/2T_c^2) (d_{T_c}/d\sigma) )</td>
<td>( 3.8 \times 10^{-4} )</td>
<td>2.56</td>
</tr>
</tbody>
</table>

the same function fits all quantities well and that the
assumption of Eq. (3) is justified. In turn, this allows the
prefactors in the Testardi and Ehrenfest relations to be
unambiguously determined, which had not previously
been possible for a phase transition in a quasi-one-dimensional
material. In particular, comparison of the magnitude of the
specific heat and thermal expansion anomalies allows us
to find \( d_{T_c}/d\sigma_{[102]} = +0.2 \) K/kbar, close to the
observed pressure dependence [24]. Comparison with the Young’s
modulus anomaly then gives \( f_{[102]} = 250 \text{ GPa} \); this
large value is consistent with our observed resonant frequency
and the expected strong bonding along the sheets [18], but
is larger than that previously estimated [4].

Use of the CAS free energy also allows us to address
questions of the statistical mechanics of the transition. In
the CAS 3D XY model [12,22], the transition temperature
is suppressed by 3D fluctuations from its mean-field value
by \( \Delta T_c = 0.24 \Delta^2 T_c \approx 16 \text{ K} \), comparable to the width
of the region of 3D fluctuations observed with x-ray
diffraction [10]. The mean-field-like step in specific heat
is given by [23] \( \Delta c_{\text{step}} = 7.1 A_0/\bar{u} \lambda T_c \approx 4.2 \gamma T_c \),
where \( \gamma \) is the electronic specific heat coefficient [7].
This value is 3 times larger than the mean-field estimate.
The increase of the specific heat jump reflects the presence
of a pseudogap above \( T_c \) [11]; the values of \( \Delta T_c \) and \( \Delta c_{\text{step}} \)
should allow detailed tests of microscopic models of the
transition [25]. As mentioned above, the cutoff wave
vector is given by \( q_{\text{max}} = \lambda / \xi_0 = 0.6 / \xi_0 \). Since, from
x-ray scattering [10], the mean-field coherence length is
estimated as being comparable to the unit cell size in
transverse directions and a few times larger along the
conducting chains, this is a reasonable value of \( q_{\text{max}} \).

It is not clear if a value of \( \bar{u} > 1 \) is physically
meaningful. In particular, the convergence domain of the
CAS free energy has not been checked for large \( \bar{u} \) [26].
However, it may be noteworthy that very similar values of
\( \bar{u} (2.56) \) and \( \lambda (0.54) \) were obtained from fits of the
Young’s modulus at the CDW transition in the quasi-one-
dimensional metal, TaS \( _3 \) [5]. In contrast, very different
parameters were obtained for superconducting [23] and

As a further check of the CAS form of the free energy,
we consider the magnetic susceptibility, shown in Fig. 3
(inset). There is a large Curie tail at low temperature;
the susceptibility between 30 and 75 K was fitted by a
Curie-Weiss law as shown in the inset. The Curie
constant implies a magnetic impurity concentration of
\( \sim 1000 \text{ ppm} \). Since the phase transition is sharp, we feel
that most of these impurities must be heterogeneous,
e.g., in the white marbling material. The difference,
\( \chi \approx \chi_{\text{Curie-Weiss}} \), shown in Fig. 3, is similar to previously
reported results for the Pauli susceptibility [7,8,27].
In the spirit of the above analysis, if we assume that the only
parameter in \( \Delta A \) which depends on magnetic field is
\( T_c \), then

\[
\Delta \chi = - \gamma^2 \Delta A / \partial H^2 = [A_0 d^2 T_c / dH^2] d^2 g / dT^2
- [A_0 (d T_c / dH)^2] d^2 g / dT^2.
\]

By symmetry, \( d_T / dH = 0 \), so the anomaly in susceptibility
is expected to resemble that in \( d g / dT \); this is clear
in comparing Figs. 2 and 3. We used \( g \) as determined
from the CAS fit to the [102] Young’s modulus, and fitted
\( \chi \) by \( \chi = \chi_{\text{Curie-Weiss}} = k g d T / dT \) + polynomial. Results
for linear and cubic polynomial backgrounds are shown
in Fig. 3. From \( k = A_0 d^2 T_c / dH^2 \), we find \( d^2 T_c / dH^2 =
-(1.8 \pm 0.3) \times 10^{-4} \text{ K} / T^2 = -\mu_0 / 14 k_b T_c \),
which is 6 times smaller than the value obtained from mean-field
theory [28]. Again, this reflects the large suppression of
\( T_c \) by 1D fluctuations and the formation of a pseudogap.

FIG. 2. Temperature derivatives of the free energy of the
CAS 3D XY model, in arbitrary units, evaluated for \( \bar{u} = 2.46 \),
\( \lambda = 0.55 \) (solid curves) and \( \bar{u} = 2.55 \), \( \lambda = 0.66 \) (dotted curves).
All quantities are fitted by a free energy expression developed by Chen, Albright, and Sengers for a 3D XY model [22], and an internally consistent set of parameters are obtained. While the large value of $\tilde{a}$ raises a yet unresolved question about the microscopic meaningfulness of the CAS approach for CDW's, the model provides a useful fitting function from which thermodynamic properties can be unambiguously extracted for comparison with microscopic models.

We wish to thank C. P. Brock for assistance in x-ray diffraction, and R. H. McKenzie, Z. Y. Chen, and M. E. Itkis for helpful discussions. This research was supported in part by the National Science Foundation, Grants No. DMR-9300507 and No. EHR-9108764.

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[16] L. R. Testardi, Phys. Rev. B 12, 3849 (1975); see Appendix A for a direct comparison with our results.


[21] Corrections to $\Delta Y_{i}$ due to (i) thermal expansion, from Eq. (1), and (ii) taking $\Delta Y_{i} = -\gamma_{0}^{i} \Delta u_{0}$ in Eq. (5), are less than or comparable to the scatter in the data, and ignored.


[26] Z. Y. Chen (private communication).
