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Specific Heat and Resistivity Near the Order-Disorder Transition in β-Brass[*]

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The specific heat and temperature derivative of the resistivity of β brass have been simultaneously measured near its order-disorder transition and found to be proportional. An extension of the Fisher-Langer theory for magnetic transitions is used to explain the results.

Several years ago Fisher and Langer predicted that the contributions to the specific heat and temperature derivative of the electrical resistivity associated with a magnetic phase transition are proportional.[1] This prediction has been verified for the ferromagnetic transition in nickel,[2,3] but seems to fail for the antiferromagnetic transitions in chromium[4] and dysprosium,[5] at least in their polycrystalline forms.

We have chosen to investigate in detail the specific heat and resistivity near the order-disorder transition in β brass for the following reasons: (1) The temperature derivative of the resistivity is known to have the same qualitative behavior as the specific heat.[6,7] (2) The specific heat of β brass has been accurately measured[8] and can be used as a check of our results. (3) High-quality samples were available to us. (4) The Fisher-Langer theory can be applied to order-disorder transitions in binary alloys.

The ac calorimetry technique used by Ashman and Handler to measure the specific heat of β brass[8] has been extended to include a simultaneous determination of the temperature derivative of the resistivity. In this method, a small sample is periodically heated with chopped light from a quartz-iodide bulb. In the proper frequency range (19 Hz was used in this experiment), the amplitude of the temperature oscillations of the sample is inversely proportional to its specific heat. These oscillations are detected by a Chromel-Constantan thermocouple with one junction spot welded to the sample and the other attached to a heat sink at the ambient furnace temperature. The amplitude of oscillations is measured with a lock-in amplifier whose output is recorded on a multipoint chart recorder. A second Chromel-Constantan thermocouple with one junction spot welded to the sample and the other in an ice bath monitors the dc temperature of the sample. This thermocouple voltage is measured with a potentiometer using a microvoltmeter as a null detector, and recorded as a second trace on the chart recorder.

The temperature derivative of the resistivity is obtained at the same time as the specific heat by passing a constant current of 0.26 A through the sample. The voltage oscillations induced by the temperature oscillations of the sample are detected with a second lock-in amplifier and recorded as the third trace on the chart recorder. After measuring the dc voltage drop across the sample at 25°C, one has the geometry-independent quantity

$$\alpha_R(T) \equiv \frac{1}{\rho_{25^\circ\mathrm{C}}}\left(\frac{d\rho}{dT}\right)_p \simeq \frac{1}{V_{25^\circ\mathrm{C}}}\frac{\Delta V(T)}{\Delta T(T)}, \tag{1}$$

where ΔV and ΔT are the magnitudes of the voltage and temperature oscillations, respectively, at temperature T. Good temperature resolution is achieved since the rms temperature oscillations are typically 0.01°K near the transition temperature.

The sample of β brass used in this experiment was cut from the same boule used by Ashman for his specific-heat measurements.[8] It contained $52.3 \pm 0.1\%$ Cu and $47.7 \pm 0.1\%$ Zn. A sample was spark cut and thinned by mechanical and electropolishing techniques to final dimensions 6.0 mm $\times$ 1.5 mm $\times$ 0.1 mm. It was blackened with a thin layer of Aquadag graphite dispersion for maximum absorption of the light and mounted in a modified version of Ashman's sample holder.[8,9]

Results of the measurements are shown in

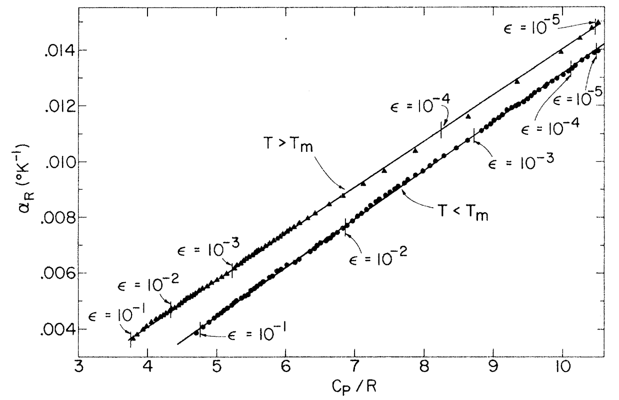

FIG. 1. Temperature derivative of resistivity versus specific heat of β-brass for data above (triangles) and below (circles) the temperature of the maxima. The lower curve has been displaced downward by 0.001°K^{-1} for clarity. Decades of ϵ are indicated by the vertical lines.

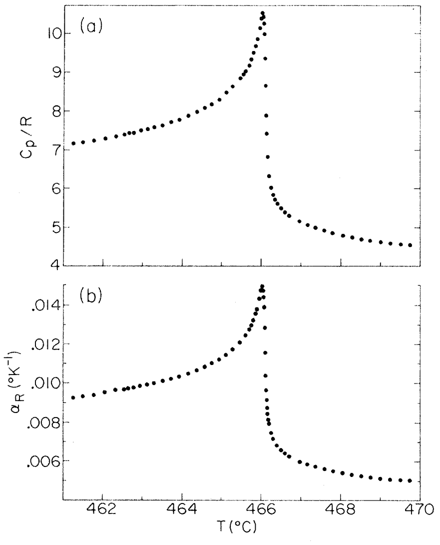

FIG. 2. (a) Specific heat of β-brass versus temperature. (b) Temperature derivative of resistivity versus temperature.

Figs. 1 and 2. In Fig. 1, C_p, normalized to Moser's data[10] at 539°C, is plotted against α_R for data above and below T_m, the temperature at which the maxima occurred. T_m was measured as 466.0 ± 1.0°C, the uncertainty being due to the calibration of the dc thermocouple. Temperatures could be measured relative to T_m with an accuracy of better than 0.002°K, since the thermoelectric power of the Chromel-Constantan pair is virtually constant in the temperature range of interest. It was therefore possible to determine that the maxima of C_p and α_R coincided to within 0.01°K.

We estimate that the normal phonon and electronic background to C_p varies by less than 0.5% of the peak value over the range of data shown in Fig. 1. The noncritical part of α_R is estimated to change by less than 1% of its peak value over the same range. Hence, the linear relationship shown on the graph indicates that the critical contributions to C_p and α_R are proportional over four decades of $\epsilon \equiv |T-T_m|/T_m$, both above and below T_m. The small deviation from linearity for $T > T_m$ and $\epsilon < 1.5\times10^{-4}$ is believed to be caused by a time-constant effect in the lock-in amplifers which appears when the signals are changing most rapidly in time. Individual plots of C_p and α_R vs T are shown in Fig. 2. We note that the relation $C_p \propto \alpha_R$ holds even within 0.04°K of the maxima ($\epsilon < 5\times10^{-5}$), where C_p and α_R are individually rounded. It is therefore likely that the same mechanism is responsible for the rounding of the two quantities.

The type of comparison shown in Fig. 1 does not depend on the assumption of a power-law divergence for C_p or α_R, nor does it require the assignment of a critical temperature. We feel that this approach is more appropriate than the standard method of testing the proportionality of C_p and α_R by comparing critical exponents.[2,3,7] Therefore, no attempt has been made to fit our data with a power-law divergence. Comparison of our C_p curve with Ashman and Handler's[8] shows good agreement, although our data are more rounded and consequently have a lower peak height. The resistivity of binary alloys has been examined recently by Bhatia and Thornton using the pseudopotential approximation.[11] Above the Debye temperature, the resistivity is given by

$$\rho = \frac{12\pi m^{*2}}{\hbar^3 e^2 k_F^{\,2}} \frac{1}{V} \int_0^1 \langle A^\dagger(q) A(q)\rangle\, x^3 dx, \tag{2}$$

where $x = q/2k_F$ and $A(q)$ is the pseudopotential matrix element for the alloy, suitably averaged over the direction of $\vec{q}$. For an alloy such as β brass it is convenient to introduce the notation $\sigma_i = \pm1$ for the occupation of the ith lattice site by an atom of Cu or Zn, respectively. Approximating the effective potentials of the individual ions by δ functions of strengths W_1 for Cu and W_2 for Zn, and assuming a rigid lattice, we may write

$$A(\vec{r}) = \tfrac{1}{2}\textstyle\sum_i [(1+\sigma_i)W_1 + (1-\sigma_i)W_2]\delta(\vec{r}-\vec{R}_i), \tag{3}$$

where the sum is taken over the lattice sites $\vec{R}_i$. The Fourier transform of (3) may be written

$$A(q) = (2\pi)^3 (N/V)\overline{W}\delta(\vec{q}) + N^{1/2}\Delta W \sigma_q, \tag{4}$$

with $\overline{W} = (W_1 + W_2)/2$, $\Delta W = (W_1 - W_2)/2$, and

$$\sigma_q = N^{-1/2} \sum_{j,\hat{q}} \exp(i\vec{q}\cdot\vec{R}_j)\sigma_j, \tag{5}$$

the sum over $\hat{q}$ denoting an average over the direction of $\vec{q}$. Substituting (4) into (2), we get an expression for the resistivity due to deviations in the average periodic potential:

$$\rho_c = \frac{12\pi m^{*2}}{\hbar^3 e^2 k_\mathrm{F}^2} \frac{N}{V} (\Delta W)^2 \int_0^1 \langle\sigma_{-q}\sigma_q\rangle x^3 dx. \tag{6}$$

Expression (6) is very similar to the contribution to the electrical resistivity from spin-disorder scattering in a magnetic system.[1] Unlike the Heisenberg ferromagnet considered by Fisher and Langer, however, there is no temperature-dependent incoherent scattering since the average potential $\overline{W}$ has no critical behavior. We also note that the appearance of energy gaps at the Fermi surface upon ordering would have a pronounced effect on the resistivity, as observed in several of the rare earths[12,13]; however, band-structure calculations in the ordered phase of β brass show no gaps at E_F attributable to the reduction in the dimensions of the zone.[14] It follows that (6) should be valid both above and below the transition temperature.

As in the spin-disorder case, the most important contributions to ρ_c arise from the scattering of electrons across the Fermi surface, that is, for $x \simeq 1$. This implies that fluctuations in the short-range order with an extent $r \lesssim k_\mathrm{F}^{-1}$ are most effective in scattering conduction electrons. Since the Fermi surface nearly fills the zone,[14] correlations between nearest neighbors will predominate.

The contribution of the short-range order in β brass to the energy density may be expressed in the Ising-model form[15]

$$U_c = -J \sum_{i,j} \langle\sigma_i\sigma_j\rangle \tag{7}$$

where the sum is taken over nearest-neighbor ion pairs. Since the nearest-neighbor correlations determine the temperature dependence of both $\rho_c(T)$ and $U_c(T)$, we are led to the same conclusion as Fisher and Langer—that $\rho_c(T) \propto U_c(T)$ and, therefore, that $\alpha_R(T) \propto C_p(T)$. It is this relation which is directly verified in Fig. 1.

We expect our results to apply to other binary alloys exhibiting second-order phase transitions, such as FeCo and Fe_3Al.[16] Further experimental work on these materials is encouraged.

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