SPECIFIC HEAT OF THE ORDER-DISORDER TRANSITION IN β BRASS*

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(Received 28 July 1969)

The specific heat C_p of β brass above and below its critical temperature $T_c = 739°K$ has been measured over the temperature range $10^{-6} < \epsilon < 10^{-1}$, where $\epsilon = |(T-T_c)/T|$. C_v was then evaluated using the Pippard relations. Above T_c, C_v is in good agreement both in magnitude and power-law dependence with Ising model calculations while below T_c, C_v depends roughly logarithmically on ϵ for $10^{-5} < \epsilon < 10^{-2}$.

Recent x-ray and neutron diffraction investigations of the order-disorder transformations in β brass[1] and Fe_3Al[2] have indicated good agreement between experimentally determined critical indices such as β, γ, and ν and relevant three-dimensional Ising-model calculations. These results strongly suggest that the specific-heat critical behavior in β brass should also be Ising-like. Another experiment[3] has indicated that the pressure dependence of T_c for various compositions of β brass may be at variance with the nearest-neighbor Ising model. However, the presence of next-nearest-neighbor interactions (which was used as a possible explanation for the variance) appears to have little effect on Ising critical behavior.[4,5]

Current theory has shed much light on the quantitative nature of the specific-heat divergence in three-dimensional Ising models. Theorists[6-8] are confident that above the T_c the specific heat for a bcc[9] lattice behaves as

$$C_v/R = 1.103\epsilon^{-1/8} + \varphi(T_c/T), \qquad (1)$$

where $\epsilon = |(T-T_c)/T|$ and where $\varphi(T_c/T)$ is roughly constant near T_c. Below T_c, the diamond structure has yielded the most information on the critical behavior of the specific heat. From the limited evidence available, it appears that C_v should depend roughly logarithmically on ϵ, at least for $4\times10^{-4} \leq \epsilon \leq 4\times10^{-2}$.[10]

The question of whether or not the above theoretical results really apply to experimental determinations of C_v and C_p for Ising-like substances has been raised by various authors.[11,12] They suggest that a "renormalization" occurs for real-world transitions and that C_v and possibly C_p attain finite cusplike behavior at T_c. Unresolved is the question over what range of ϵ ideal Ising behavior as outlined in the previous paragraph should hold. That is, will β brass exhibit a $\frac{1}{8}$th power-law divergence, characteristic of ideal Ising behavior above T_c, only for $\epsilon > 10^{-6}$, only for $\epsilon > 10^{-3}$, or possibly never?

The experimental determination of C_p vs ϵ was achieved using an ac calorimetry technique similar to that used for Ni.[13] The basis of this technique is the fact that if a sample of appropriate size is periodically heated at a proper frequency, the amplitude of the sample's periodic temperature variation is inversely proportional to its heat capacity.

Single crystal β-brass samples were cut in 16-mil thicknesses from a high-quality boule[14] before being etched in HNO_3 to 6 mil $\times$ 60 mil $\times$ 60 mil final dimensions. Chromel and constantan thermocouple wires of 0.7 mil diam were then gently spot welded to one face of the sample in order to form two thermocouple hot junctions, one for the lock-in signal (a measure of the sample's periodic temperature variation ΔT) and the other for the dc thermocouple voltage (a measure of the sample's average temperature T). The opposite, light-absorbing face was coated with Aquadag to eliminate the effect of possible optical absorption differences between the ordered and disordered states of β brass. Since at elevated temperatures β brass both oxidizes and loses Zn via sublimation, the sample chamber was filled with additional β brass to maintain a Zn-saturated atmosphere. The sample cahmber was also sealed and filled with N_2 having approximately atmospheric pressure at T_c.

A mathematical analysis of the sample's temperature response to square-wave heating at frequency ω has revealed that $\Delta T \propto 1/C_p$ with less than a 1% error for 5 Hz $\leq \omega \leq$ 25 Hz. That is, in this frequency range errors due to the finite size of the thermocouple wires, the thermal coupling between the sample and its surroundings, and the sample's inability to reach internal thermal equilibrium are less than 1% of ΔT.

To test the frequency range 5 Hz $\leq \omega \leq$ 25 Hz, we obtained x-y recorder plots of ΔT vs T like the one shown in Fig. 1. Changing ω between runs, we normalized the ΔT signal at one point to a previous plot prior to each run and alter-

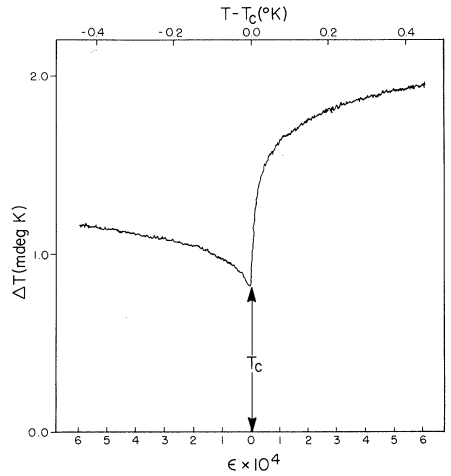

FIG. 1. An x-y recorder plot of ΔT vs T over a range of 0.45°K on either side of the critical temperature T_c with $\epsilon = |(T-T_c)/T|$.

nately heated and cooled through T_c to obtain the plots themselves. The curves obtained overlap one another so well that any of them could be used to represent the data. The frequency independence of the shapes of these curves indicated that $\Delta T \propto 1/C_p$ for 5 Hz $\leq \omega \leq$ 25 Hz and also demonstrated that atomic diffusion must equilibrate β-brass's state of order in time τ with $\omega\tau \ll 1$ since, if $\omega\tau \approx 1$, the shape of the graphs of ΔT vs T would be highly frequency dependent. The ΔT vs T results were sample independent except for differences in the rounding of the transition for $\epsilon < 5\times10^{-5}$. Figure 1 displays these results for the sample giving the least rounding.

The relative C_p data obtained from the ΔT vs T curves were normalized at 810°K to Moser's absolute C_p determinations[15] (they subsequently agreed very well with the rest of his data). Using the thermodynamic equality $C_p - C_v = TV\beta^2/K_T$ and the Pippard relations,[16] $C_p = \xi VT\beta + K_1$ and $K_T = \beta/\xi + K_2$, the critical behavior of C_v was determined from our knowledge of C_p vs ϵ, i.e.,

$$C_v = C_p - (C_p - K_1)^2/[(C_p - K_1) + \xi^2 TVK_2]. \quad (2)$$

(The first of the Pippard relations has been shown to hold for β brass,[17] and we see no reason to doubt the applicability of the second.) The constants K_1 and K_2 were obtained from the pertinent thermal expansion data[18,19] and the isothermal compressibility values given by Yoon[3] while ξ, the slope of the λ line, has already been accurately determined.[3] The values appear to be $K_1 = (0.48 \pm 0.65)R$, $K_2 = (9.18 \pm 0.92)\times 10^{-7}$/bar, and $\xi = 625 \pm 10$ bar/°K. Since C_v differs significantly from C_p near T_c (e.g., C_p is 30%

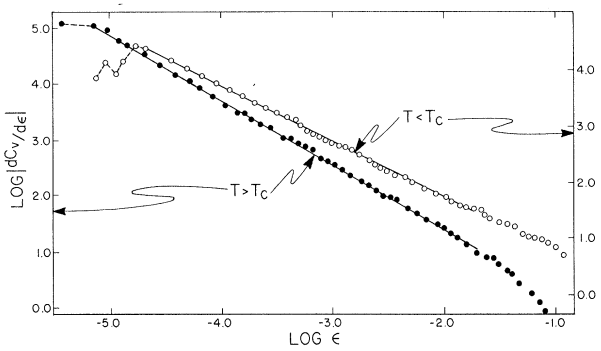

FIG. 2. Plot of $\log|dC_v/d\epsilon|$ vs $\log\epsilon$. The solid lines are linear fits to the data points encompassed by them. The two vertical axes are slightly displaced from one another but do have the same scale so that the different slopes for $T > T_c$ and $T < T_c$ imply that $\alpha \neq \alpha'$.

larger than C_v at $\epsilon \approx 10^{-5}$ for $T > T_c$), the above conversion to C_v is necessary for an accurate comparison with theory.

If C_v of Eq. (2) has the power-law form $C_v = A\epsilon^{-\alpha} + B$ for $T > T_c$,[20] as Eq. (1) suggests, then

$$\log|dC_v/d\epsilon| = -(1+\alpha')\log\epsilon + \log|A'|. \quad (3)$$

A $\log|dC_v/d\epsilon|$ vs $\log\epsilon$ plot will then be a straight line with slope $-(1+\alpha)$ and y intercept $\log|\alpha A|$.[13] Conversely, if such a plot is a straight line, then C_v has this power-law dependence. Similarly, if $C_v = (A'/\alpha')(\epsilon^{-\alpha'} - 1) + B'$ for $T < T_c$,[20] then

$$\log|dC_v/d\epsilon| = -(1+\alpha')\log\epsilon + \log|A'|. \quad (4)$$

This fitting of the data by Eqs. (3) and (4) removes the need to know B, B', or the magnitude of the lattice and electronic contributions to the specific heat. In addition, analysis of the data has shown that the values of α and A as well as α' and A' obtained from the least-squares fitting of straight lines to the relevant $\log|dC_v/d\epsilon|$ vs $\log\epsilon$ plots are relatively insensitive to possible variations in K_1, K_2, and ξ.

As the rounding of the transition is so small (see Fig. 1), most of the data are unaffected by the small uncertainty in T_c. T_c itself was chosen to obtain the best straight-line fits to all the data. The fact that this T_c is only 0.5 mdeg K ($\epsilon \approx 10^{-6}$) below the best-fit T_c for the $T > T_c$ data alone and only 0.5 mdeg K ($\epsilon \approx 10^{-6}$) above the best-fit T_c for the $T < T_c$ data is very reassuring. As seen in Fig. 1, T_c also lies within the rounding of the transition.

Figure 2 displays the $\log|dC_v/d\epsilon|$ vs $\log\epsilon$ results and their least-squares straight-line fits. The values of α, A, α', and A' obtained from these these fits together with their standard deviations as error limits are displayed in Table I (of course,

Table I. Values of α, A, α', and A' for the expressions $C_V = A\epsilon^{-\alpha} + B$ and $C_V = (A'/\alpha')(\epsilon^{-\alpha} - 1) + B'$.

$T > T_c$	Eq. (1)	$T < T_c$
$\alpha = 0.13 \pm 0.01$	$\alpha = 0.125$	$\alpha' = -0.01 \pm 0.01$
$A = (1.09 \pm 0.09)R$	$A = 1.103R$	$A' = (0.53 \pm 0.04)R$

the values of A and A' depend on the normalization of C_p to Moser's data, but the error involved in this normalization is much less than the standard deviation of the least-squares fit). A comparison of the α's and of the A's shows that the experimental data for $T > T_c$ agree extremely well with the predictions of Eq. (1). That is, not only α but also A serves as a basis of comparison between theory and experiment. Since our data display a positive α, renormalization with its characteristic nonpositive α[11] cannot apply for $T > T_c$ and $\epsilon \geq 10^{-5}$. Column 3 of Table I indicates that $\alpha' \approx 0$, so that $C_V \approx -A' \ln\epsilon + B'$ provides a good representation of our data for $T < T_c$. The good agreement between theory and the experimental results above T_c suggests that the experimental data below T_c are also Ising-like. Thus, when firmly established, the Ising model results below T_c should be close to logarithmic in ϵ, at least over the range $2 \times 10^{-5} \leq \epsilon \leq 2 \times 10^{-2}$.

*Work supported by the U. S. Army Research Office (Durham) under Contract No. DA-HC04-67-C-0025 and by the Advanced Research Projects Agency under Contract No. SD-131.

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MAGNETOELECTRIC EVIDENCE FOR THE ATTAINABILITY OF TIME-REVERSED ANTIFERROMAGNETIC CONFIGURATIONS BY METAMAGNETIC TRANSITIONS IN $DyPO_4$

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(Received 23 July 1969)

The experimental observation and an atomic mechanism of the linear magnetoelectric effect in $DyPO_4$ are reported and shown to provide evidence for the feasibility of isothermal forced switching between time-reversed (i.e., moment-reversed) antiferromagnetic configurations by means of metamagnetic transitions.

This Letter reports the observation of the linear magnetoelectric (ME) effect in $DyPO_4$, an antiferromagnet in which the application of a static magnetic field H along the antiferromagnetic axis causes a metamagnetic (i.e., relatively abrupt) transition of the ionic magnetic moments from an initially antiparallel configuration A_I to a parallel configuration. It should be noted that this is the first study of the influence of metamagnetic transitions on the magnetoelectric