

## Low-Temperature Specific Heats of the $\beta'$ and $\zeta^0$ Phases in Equiatomic AgZn<sup>†</sup>

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Heat-capacity measurements between 1.3 and 4.2 °K have been made on equiatomic AgZn in both the  $\beta'$  and  $\zeta^0$  phases. Significant differences were found in the Debye temperature and the electronic specific-heat coefficient, the latter data being discussed in terms of Fermi-surface-Brillouin-zone interactions. Furthermore, it is concluded that  $\beta'$  is the stable phase at 0 °K, and that in this particular alloy, vibrational properties are of major importance in controlling phase stability near 0 °K.

In the equiatomic AgZn alloy two phases can be retained at room temperature: the  $\beta'$  phase with a fully ordered CsCl structure and the partially disordered  $\zeta^0$  phase which has a complex hexagonal structure.<sup>1</sup>

Neither the  $\beta'$  nor the  $\zeta^0$  phase appears to transform martensitically upon cooling to liquid-helium temperatures.<sup>2</sup> This offers the rather rare possibility of comparing the experimental values of the electronic density of states at the Fermi level for two different structures of an alloy of the same composition, by measuring the low-temperature specific heat.

In our experiment, a polycrystalline Ag-50-at.% Zn cylinder 1.4 cm in diam and 2.5 cm long was used. By quenching from 400 °C, or annealing at 240 °C, and cooling to room temperature the same sample was obtained either in the  $\beta'$  or in the  $\zeta^0$  phase.<sup>1</sup>

The specific heats were measured in a standard adiabatic calorimeter covering the temperature range between 1.3 and 4.2 °K.

In Fig. 1, the experimental values of  $C/T$  versus  $T^2$  for  $\beta'$  and  $\zeta^0$  are shown. The plotted lines represent the least-squares fitting to the usual relation

$$C/T = \gamma + AT^2 + BT^4,$$

where  $\gamma$ ,  $A$ , and  $B$  are constants,  $\gamma$  being the electronic specific-heat coefficient, and  $A = 2.4\pi^4 R \Theta_0^{-3}$ , where  $R$  is the molar gas constant and  $\Theta_0$  is the limiting Debye temperature. The values of  $\gamma$ ,  $A$ ,  $B$ , and  $\Theta_0$  obtained for each phase are given in Table I.

The free-electron value  $\gamma_F$  of the electronic specific-heat coefficient for our composition is given by

$$\gamma_F = 0.111 \Omega^{2/3} \text{ (mJ mole}^{-1} \text{ deg}^{-2}\text{)},$$

where  $\Omega$  is the volume per atom in the alloy expressed in  $\text{\AA}^3$ .

Using the value 3.140  $\text{\AA}$  for the lattice parameter

of the  $\beta'$  phase at 0 °K,<sup>3</sup>  $\gamma_F(\beta') = 0.689 \text{ mJ mole}^{-1} \text{ deg}^{-2}$  is obtained. Hence, for the  $\beta'$  phase,  $\gamma/\gamma_F = 1.03$ , which suggests that in this phase the conduction electrons behave as nearly free electrons with small band gaps across the {110} Brillouin zone where contact with the Fermi sphere occurs. A similar conclusion is obtained from band-structure calculations.<sup>4</sup>

For the  $\zeta^0$  phase, no band calculation exists as far as the authors know. Since the difference in volume per atom between the two phases is calculated<sup>5</sup> to be about 0.7%, the decrease of the  $\gamma$  value from  $\beta'$  to  $\zeta^0$  cannot be explained as due to a change in electron density. For the  $\zeta^0$  phase,  $\gamma/\gamma_F = 0.86$ . The Brillouin zone for the  $\zeta^0$  phase

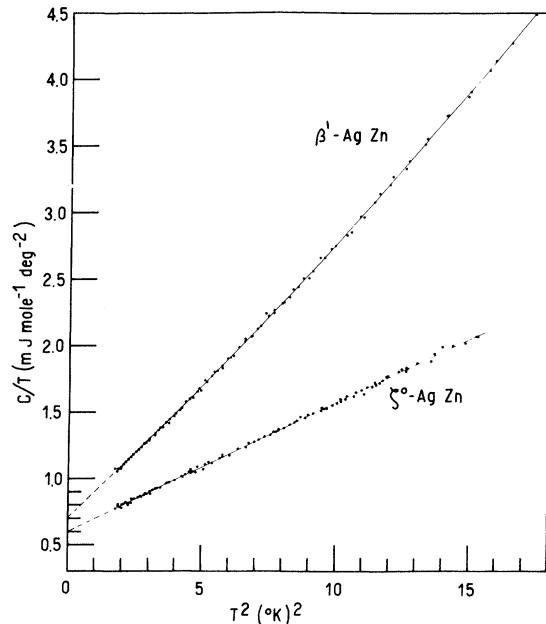


FIG. 1. Plots of  $C/T$  versus  $T^2$  for the  $\beta'$  and  $\zeta^0$  phases of equiatomic AgZn.

TABLE I. Values<sup>a</sup> of  $\gamma$ ,  $A$ , and  $B$  in the relation  $C/T = \gamma + AT^2 + BT^4$  for the  $\beta'$  and  $\zeta^0$  phases of equiatomic AgZn, and values of  $\Theta_0 = (2.4\pi^4 R/A)^{1/3}$ .

Phase	$\gamma$ (mJ mole <sup>-1</sup> deg <sup>-2</sup> )	$A$ (mJ mole <sup>-1</sup> deg <sup>-4</sup> )	$\Theta_0$ (°K)	$B$ (mJ mole <sup>-1</sup> deg <sup>-6</sup> )
$\beta'$	0.708 ± 0.006	0.190 ± 0.001	217.1	0.0016 ± 0.0001
$\zeta^0$	0.597 ± 0.006	0.100 ± 0.001	268.9	-0.0002 ± 0.0001

<sup>a</sup>The errors indicated are standard deviations calculated from the least-squares fit.

can be obtained by a small distortion of the {110} Brillouin zone of  $\beta'$ .<sup>6</sup> Since the volume in reciprocal space remains constant upon distortion, contact between the Fermi sphere and the  $\zeta^0$  Brillouin zone occurs at a lower electron concentration than for the  $\beta'$  phase. It is probable, then, that our low  $\gamma/\gamma_F$  value for  $\zeta^0$  is due to the drop in the density of states after contact.

Table I shows that the limiting Debye temperature for the  $\zeta^0$  phase is much larger than that of the  $\beta'$  phase. Assuming that the difference  $\Delta\Theta$  does not change much with temperature, the increase in zero-point vibrational energy between  $\beta'$  and  $\zeta^0$  can be estimated according to  $\Delta E_{z.p.} = \frac{3}{8}R\Delta\Theta_0$ , this gives  $\Delta E_{z.p.} = 116$  cal mole<sup>-1</sup>.

The difference between the total electronic energy in  $\beta'$  and  $\zeta^0$  can be estimated as follows. It is known experimentally that the heat of formation

of  $\beta'$  is about 50 cal mole<sup>-1</sup> more exothermic than that of the  $\zeta^0$  phase at 324 °K.<sup>7</sup> Since in the harmonic approximation above the Debye temperature the vibrational energy of any solid including the zero-point motion is very nearly  $3RT$ , the vibrational contribution to the difference in the heat of formation of  $\beta'$  and  $\zeta^0$  should be small.<sup>8</sup> In turn, this implies that the 50 cal mole<sup>-1</sup> are mainly due to the difference between the total energy of the electrons in each phase.

These differences of electronic and zero-point vibrational energies between  $\beta'$  and  $\zeta^0$  indicate that  $\beta'$  is the stable phase at 0 °K, and that in this particular alloy vibrational properties are of major importance in controlling phase stability near 0 °K.

Recently, a similar experiment has been done at the Nagoya University in Japan, for an alloy containing 46-at.% Zn in Ag.<sup>9</sup>  $\gamma$  was found to be equal in both  $\beta'$  and  $\zeta^0$  phases with a value of 0.62 mJ mole<sup>-1</sup> deg<sup>-2</sup>, while the Debye temperatures were very different.

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<sup>8</sup>This contribution is calculated to be 23 cal mole<sup>-1</sup> within the Debye model.

<sup>9</sup>S. Noguchi (private communication).