Rigid-Band Behavior in Aluminum-Based Alloys—Electronic Specific Heat

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Measurements of the specific heat of aluminum and its dilute alloys below 4°K show that the electronic specific-heat coefficient γ changes linearly with the valence electron concentration from below to above the pure-aluminum value, in contradiction to previous work. The difference is attributed to undetected precipitation of the solutes Ge or Si in the previous work. Good agreement is found between γ values for AlZn alloys and the previous AlMg alloys. The rate of increase of γ is three times that expected from free-electron theory. For pure Al, $\gamma = 1.362$ mJ mole^{-1} °K^{-2}, and the Debye temperature $= 431$°K.

INTRODUCTION

IF the electronic specific-heat coefficient γ of a dilute alloy measures the density of states of the host metal at an energy displaced from the Fermi energy of the host by a calculable amount, then energy displacements in opposite directions should give rise to shifts in γ in opposite directions,[1] barring the unlikely coincidence that the density of states has an extremum at the Fermi energy of the pure host metal. Hopes for such simple behavior were, however, dashed by the experiment of Guthrie,[2] who compared the effects of adding zinc and nickel, separately as well as together, to copper. If zinc merely adds electrons to the conduction band of copper and nickel takes them away, the displacements of the Fermi energy should be in opposite directions, and and simultaneous additions of both (in appropriate amounts) should leave the Fermi energy unchanged. The experimental result was that either solute raises the value of γ and that the increases are independent when both are added. Precisely the same effect was found in silver by Montgomery and Pells,[3] who investigated the Ag-Pd-Cd system. This behavior has led naturally to the speculation that the dominant variable controlling the phenomenon was the electronic mean free path, not the electron-per-atom ratio e/a.

This speculation was supported by the recent finding by Blythe, Holden, Dixon and Hoare[4] that aluminum, too, exhibited the cusp effect, with the difference that either magnesium ($Z' = -1$) or silicon ($Z' = +1$) or germanium ($Z' = +1$) additions depressed the value of γ in aluminum. The present paper reports our measurements on aluminum plus either zinc ($Z' = -1$) or germanium or both which contradict this finding. We find that γ increases smoothly with electron concentration through the pure aluminum value, and that simultaneous addition of zinc and germanium in equal amounts yields a γ value indistinguishable from that of

pure aluminum. We speculate that the contrary result of Blythe and co-workers is due to undetected precipitation of the quadrivalent solutes in their samples.

Our result suggests that the rigid-band model is still a good guide to alloy behavior at small concentrations in suitably simple metals, and that the cause of the cusp effect in the noble metals lies in some feature peculiar to themselves.

PROCEDURE AND RESULTS

The measurements were made in the calorimeter previously used in our noble-metal-alloy work.[5] The technique consists of measuring repeatedly the time a sample requires to warm between fixed temperatures under continuous heating. Details may be found in our previous publications.

The samples were prepared for us by J. P. G. Shepherd, Case Institute, who chill cast them under argon. Spectroscopic analysis showed that the total concentration of paramagnetic impurities was generally under 10 ppm. For the AlGe alloys, care must be taken that the Ge does not precipitate, since the solution is unstable at room temperature. To verify that the chill-casting procedure was successful in freezing in the germanium, lattice parameter measurements were made for us by C. E. Lowell at the National Aeronautics and Space Administration Lewis Research Center, who found at 20°C:

pure Al:	4.0504 Å
98% Al–2% Ge:	4.0541 Å

which agree with the measurements of Axon and Hume-Rothery[6] for the solid solution. The measurements were made from the cut faces of unused parts of the ingots adjacent to the parts used for samples. We believe this procedure to give results more characteristic of the bulk than the procedure followed by Blythe, who measured lattice parameters from filings taken from the ex-

[1] This presumes the well-known rigid-band model. See, for example, H. Jones, Proc. Roy. Soc. (London) 49, 250 (1937).

[2] G. L. Guthrie, Phys. Rev. 113, 793 (1959).

[3] H. Montgomery and G. P. Pells, in Proceedings of a Conference on the Electronic Structure of Alloys, University of Sheffield, 1963 (unpublished).

[4] H. J. Blythe, T. M. Holden, M. Dixon, and F. E. Hoare, Phil. Mag. 11, 235 (1965).

[5] B. A. Green, Jr., and A. A. Valladares, Phys. Rev. 142, 379 (1966); B. A. Green, Jr., and H. V. Culbert, *ibid.* 137, A1168 (1965).

[6] H. J. Axon and W. Hume-Rothery, Proc. Roy. Soc. (London) A193, 1 (1948).

TABLE I. Low-temperature specific heats of
aluminum-based alloys.

e/a	Composition at.%	γ mJ mole^{-1}°K^{-2}	θ_D °K
3.000	100.0 Al	1.362	431
2.978	2.2 Zn	1.347	423
2.925	7.5 Zn	1.330	401
2.884	11.6 Zn	1.278	372
3.010	1.0 Ge	1.366	472
3.020	2.0 Ge	1.369	425
3.000	1.0 Zn 1.0 Ge	1.360	415
Mean standard deviation		0.003	1

terior surface of his samples, the filings then being
strain-annealed.

The molar specific heat was in all cases satisfactorily
fitted by the usual relation

$$C = \gamma T + \alpha T^3.$$

The coefficient α is related to the Debye temperature
at absolute zero Θ_0 by

$$\alpha = (12/5)\pi^4 R \Theta_0^{-3}.$$

The results are reported in terms of γ and Θ_0 in Table
I, and the γ values are compared with those of Ref. 4
in Fig. 1. The agreement for pure aluminum is quite
good, as is that for e/a less than 3.00. This agreement
is especially interesting since we compare the solute Zn
with the solute Mg, which differs considerably from Zn
in mass and, presumably, in ionic potential, and agrees
only in valence.

For e/a greater than 3.00, the disagreement between
the present results and those of Ref. 4 is evident from
Fig. 1. We note that the rate of decrease found by
Blythe *et al.* is only slightly less than that expected if
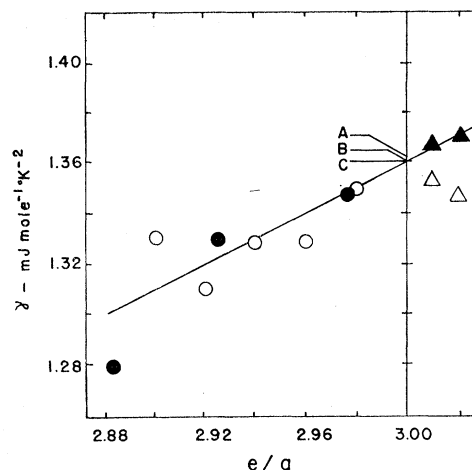one assumes that the solute is completely precipitated

FIG. 1. Electronic specific-heat coefficient γ versus valence-
electron concentration e/a for aluminum-based alloys. The present
data are indicated by black circles (AlZn), black triangles (AlGe),
point A (pure Al), and point B (98%Al–1%Zn–1%Ge). The
other data are from Ref. 4 and represent alloys as follows: open
circles (AlMg), point C (pure Al), and open triangles (AlGe). The
standard deviation of the present data is given by the size of the
symbols.

as the pure element, contributing nothing to the elec-
tronic specific heat.

The rate of rise of γ with e/a is approximately three
times what one would expect for free electrons. For a
gas of free electrons one expects

$$\frac{d(\ln\gamma)}{d(\ln e/a)} = \frac{1}{3},$$

whereas the observed value is closer to unity. The excess
is not likely to be a band-structure effect, being much
too large. We have no other interpretation to offer.