Low-Temperature Specific Heat of Ni-Base fcc Solid Solutions with Cu, Zn, Al, Si, and Sb

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For Ni–Cu solid solutions around the equiatomic composition the low-temperature specific-heat term linear in temperature was found to contain a magnetic contribution. The measured γ for these alloys is, therefore, not representative of the electronic specific heat. The presence of magnetic moments in Ni–Cu alloys with Cu contents as high as 0.6 atomic fraction may be concluded from the known magnetic properties, as well as from the low-temperature specific-heat results. The γ values for the Ni–Zn alloys vary with the electron concentration in a manner analogous to that observed for Ni–Cu alloys, although the available data are much more limited.

INTRODUCTION

IN solid solutions of Ni with Cu, Zn, Al, and Si, the magnetic saturation moment decreases with increasing solute content. This behavior has been considered as an indication of filling up of the d band of Ni by the valence electrons of the solute elements. On this picture, one would expect the electronic specific heat coefficient, which is a measure of the density of states at the Fermi surface, $N(E_F)$, to decrease from the high value for Ni to a low value approximately corresponding to that of Cu, with a filled $3d$ band, for alloys containing the above solutes in concentrations sufficient to decrease the saturation moment to zero. For Ni-Cu alloys the coefficient γ of the low-temperature specific heat term linear in temperature shows a decrease with increasing Cu content up to[1] 0.38 atomic fraction Cu but, for alloys containing 0.60 Cu, or more, the γ values[1,2] are much higher than expected, and the two sets of data points do not appear to join each other smoothly. No information is available for the concentration range between 0.40 and 0.60 atomic fraction Cu, and no low-temperature specific-heat data were published for fcc solid solution alloys of Ni with nontransition elements other than copper. The present investigation was undertaken to provide such data and to attempt a clarification of the origin of the unexpectedly high γ values for certain Ni-Cu alloys.

EXPERIMENTAL PROCEDURE

Except for the Ni-Zn alloys, all specimens were induction melted in recrystallized alumina crucibles in an argon atmosphere. Electrolytic nickel with 0.7% Co max, 0.01% Fe, 0.01% Cu, and 0.001% S was used. The copper was 99.999% pure. The silicon was a 99.8% grade. The Ni-Zn alloys were kindly furnished by Dr. E. V. Clougherty and Dr. L. Kaufman of Manlabs, Inc., who prepared them by prolonged heating at 1300°C in evacuated and sealed silica tubes. The induction-melted alloys were homogenized at 1000°C (the temperature was 1200° for the Ni-Si alloys) for 72 h in an atmosphere consisting of 92% He+8% H_2, and then water quenched. Metallographic examination showed the homogenized alloys to consist of a single phase. Table I gives the chemical analysis of each alloy for the component elements. Spectrographic analysis showed the Cr, Co, and Fe content of the alloys to be of the order of 0.01%.

TABLE I. Specific heat results for fcc Ni-base solid solution alloys.

Alloy composition	A in 10^{-4} cal mole^{-1} deg^{-1}	γ in 10^{-4} cal mole^{-1} deg^{-2}	rms dev	θ_D in °K
$Ni_{0.901}Cu_{0.099}$	0	16.8		388
$Ni_{0.55}Cu_{0.45}$	2.59	15.6		336
$Ni_{0.478}Cu_{0.522}$	5.65	17.5		389
$Ni_{0.478}Cu_{0.522}$[a]	5.75	16.9	0.20	346
$Ni_{0.478}Cu_{0.522}$[b]	4.15	15.6	0.22	321
$Ni_{0.45}Cu_{0.55}$	10.44	16.2	0.35	593
$Ni_{0.45}Cu_{0.55}$[c]	10.43	16.38	0.35	380
$Ni_{0.907}Zn_{0.093}$	2.30	15.5	0.25	333
$Ni_{0.815}Zn_{0.185}$	1.79	18.1	0.12	387
$Ni_{0.742}Zn_{0.258}$	8.14	18.5	0.21	317
$Ni_{0.903}Al_{0.097}$	2.36	16.3	0.13	338
$Ni_{0.961}Si_{0.039}$	1.94	17.1	0.17	366
$Ni_{0.92}Si_{0.08}$	1.68	17.9	0.19	345
$Ni_{0.96}Sb_{0.04}$	4.22	18.1	0.19	318
$Ni_{0.919}Sb_{0.081}$	4.40	18.5	0.25	287

[a] Cooled in a magnetic field, no field, applied during the measurements
[b] Cooled in a magnetic field and measurements made in magnetic field.
[c] Least-squares solution for A and γ, with the Debye temperature fixed at $\theta_D = 380$°K.

The specific-heat measurements were carried out between 1.3 and 4.2°K, with the procedure described previously.[3] In each experiment the carbon-resistor thermometer was calibrated against the vapor pressure of liquid He, using the 1958 He vapor pressure-temperature tables. The usual two-parameter equation $(\ln R/T)^{1/2} = B \ln R + A$ satisfactorily represented the temperature-resistance relationship for the carbon thermometer between 1.3 and 4.2°K. The $Ni_{0.48}Cu_{0.52}$ alloy was also measured after cooling from room temperature to 1.3°K in a magnetic field of 14 kOe; specific-heat measure-

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ments were made both with and without the magnetic field on during the measurement. The carbon thermometer was, in this case, calibrated both without and with the magnetic field on, but no difference was observed.

RESULTS

The specific-heat data for the Ni-base solid solution alloys are shown in Figs. 1 and 2. Considerable deviations from linearity occur in C/T versus T^2 in the low-temperature region. Such specific-heat anomalies were previously observed in the Ni-Cu alloys containing more than 40% Cu.[2] Wohlfarth[4] noted years ago that the low-temperature magnetic susceptibilities for Cu-rich Ni-Cu alloys[5] are much too high to be reconcilable with

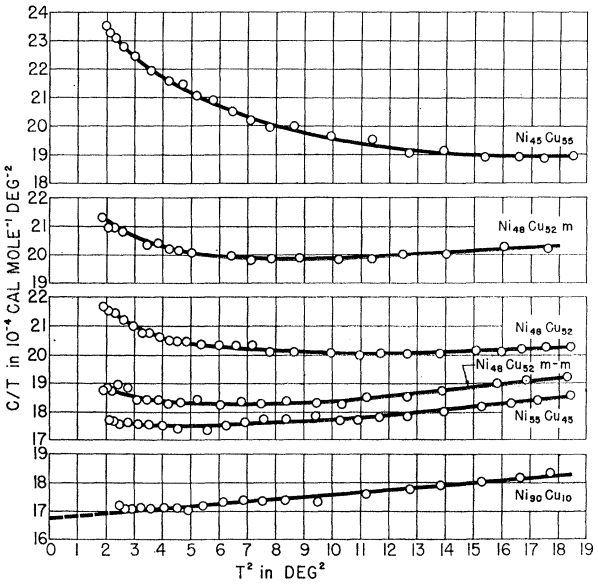

FIG. 1. Low-temperature specific heat of Ni-Cu solid solution alloys. For alloy $Ni_{0.48}Cu_{0.52}$, data were obtained both without magnetic cooling and after magnetic cooling from room temperature to 4.2°K with the magnetic field turned off during the measurements (m) and after magnetic cooling with the magnetic field on during the measurements (m-m).

the usual interpretation of the band structure of these alloys. It was suggested by him that inhomogeneous nickel distribution in these alloys, and the attendant formation of ferromagnetic "islands" or clusters, may be responsible for the effect. The magnetic cluster interpretation was subsequently strongly supported by susceptibility measurements with neutron irradiated Ni-Cu alloys[6] and by Schröder's analysis[7] of the low-temperature specific-heat anomaly.[2] In the present work, this analysis was successfully applied over the range of Cu concentrations from 0.45 to 0.55 (Figs. 1, 3). The sets of corresponding C and T values determined for each

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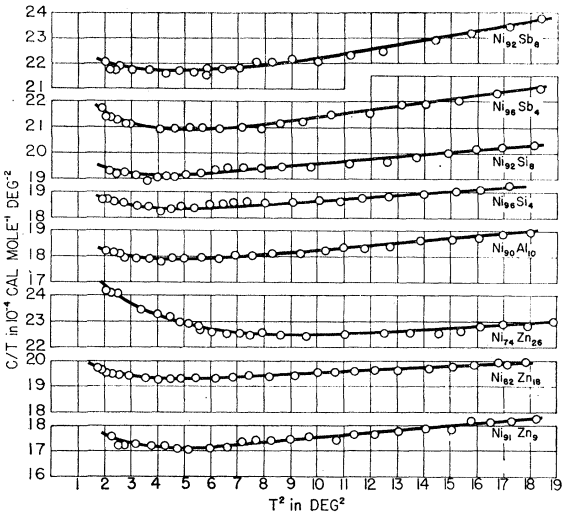

FIG. 2. Low-temperature specific heat of Ni-base fcc solid solutions with Zn, Al, Si, and Sb.

alloy were used to solve the modified specific heat formula: $C=A+\gamma T+\beta T^3$ by a least-squares method for the parameters A, γ, and β, where A is the magnetic cluster specific heat.[7] The $(C-A)/T$ versus T^2 graphs for the various alloys are shown in Figs. 3 and 4. As seen in Table I, A was found to increase with the Cu-content in the composition range studied. The anomalies for the Ni-Zn alloys may be interpreted in a similar way, and they show a general increase of the magnetic cluster specific heat with the zinc content.[8]

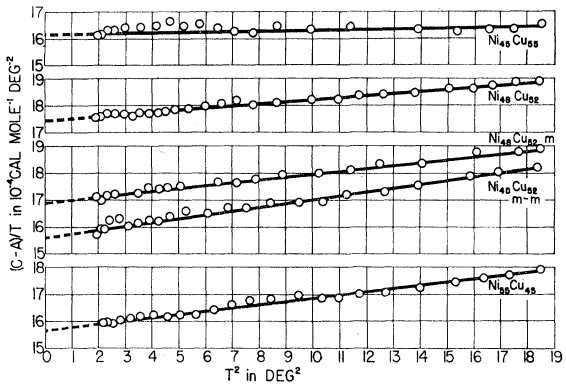

FIG. 3. $(C-A)/T$ versus T^2 for Ni-Cu solid solution alloys. m designates line for measurements made after magnetic cooling from room temperature to 4.2°K, with the magnetic field turned off during the measurements. $m-m$ designates line for measurements made after magnetic cooling from room temperature to 4.2°K, with the magnetic field on during the measurements.

[8] The fact that the A value for the alloy with the lowest zinc content is somewhat higher than expected may be due to the effect on the least-squares calculation of the lowest temperature data point, which represents an abnormally high specific heat, possibly as a result of the re-evaporation of He adsorbed at the specimen surface. Because of this adsorption effect, which is often important when exchange gas is used for heat transfer, the lowest magnetic cluster specific heat values listed in Table I are relatively unreliable.

It should be noted that the β coefficients resulting from the above least-squares solution of the three-term specific heat equation, and the Debye temperatures θ_D calculated from them, are not very reliable. For instance, $\theta_D = 593°K$ for $Ni_{0.45}Cu_{0.55}$ is unreasonably high. It was found, however, that setting $\theta_D = 380°K$ and finding the least-squares solution for A and γ results in values only slightly different from those obtained by the unrestricted θ_D calculation, Table I. The root mean square deviation for this solution with fixed θ_D is 0.35, negligibly different from the rms deviation for the solution with unrestricted Debye temperature. Clearly, the least-squares solution of the three-term specific-heat equation is quite insensitive to appreciable changes in the Debye temperature. The latter is, therefore, not reliably determined. The significant fact is, however, that this uncertainty of the Debye temperature has practically no effect on the γ value.

DISCUSSION

The early interpretation[9] of the band structure of Ni-Cu alloys was based on the concept of filling up of the 3-d band of Ni by the valence electrons of Cu. Using a gyromagnetic ratio for nickel of $g = 2.183$, the saturation magnetization value of 0.6 for nickel leads to a spin moment per atom of $0.55\mu_B$. In reasonably good agreement with the assumption that, on alloying, each copper atom contributes one electron to filling up the 0.55 vacancies in the d band of Ni, the initial slope of the saturation moment versus Cu-concentration line extrapolates to zero moment at a copper concentration of 0.53.[10,11] However, this interpretation appears to be contradicted by the low-temperature specific-heat results. The γ values obtained for the Cu-rich alloys by Guthrie, Friedberg, and Goldman,[2] Manchester[12] and the present investigation (Table I) suggest density of states values far too high in comparison with those to be expected for alloys with a filled d band. In a recent study of the low-temperature specific heat of various fcc solid solution alloys of 0-3d transition elements[13,14] it was concluded that the measured γ values often comprise an important contribution of magnetic origin. The theoretical possibility of such a contribution was first suggested by Overhauser[15] for antiferromagnets. It was

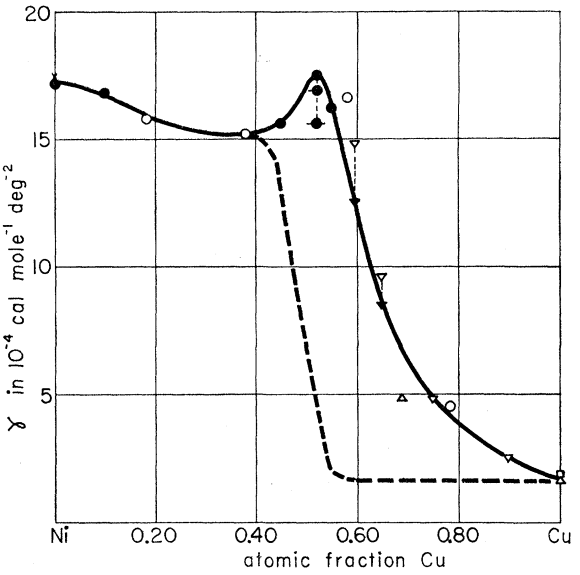

FIG. 5. Coefficient γ of low-temperature specific-heat term linear in temperature for Ni-Cu alloys. Data points • obtained in the present investigation. The stroke on the left indicates results after magnetic cooling with the field turned off during the measurements, whereas the point with strokes on both sides represents results obtained after magnetic cooling, with the magnetic field on during the measurements. Data points ○ are from Ref. 1. Points ▽ show values from Ref. 2. Data points ▼ were calculated from the measured values Ref. 2, with correction for magnetic cluster specific heat Ref. 7. Points △ are from Ref. 11.

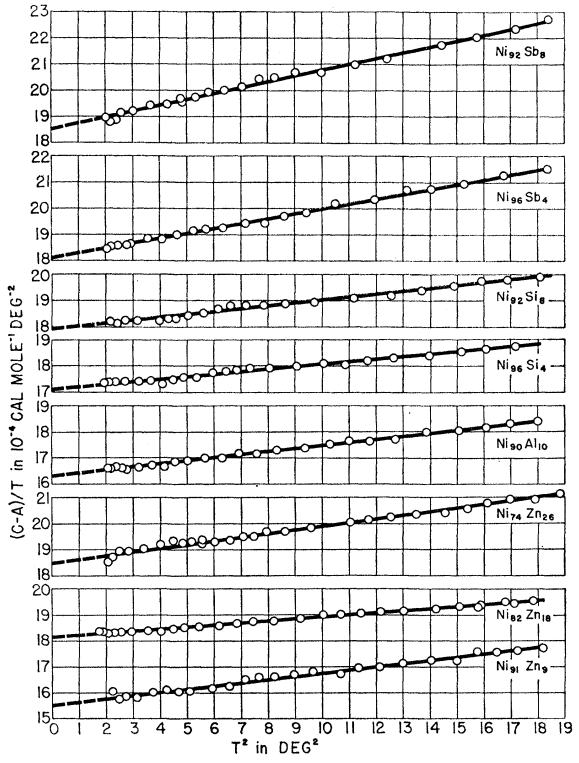

FIG. 4. $(C-A)/T^2$ for Ni-base fcc solid solution alloys with Zn, Al, Si, and Sb.

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shown by Marshall[16] that the occurrence of a magnetic contribution to the low-temperature specific-heat term linear in temperature does not necessarily require an antiferromagnetic structure. He pointed out that the condition for this effect, namely that a sufficiently large number of spins be located in a near-zero field, may be satisfied in dilute alloys, where localized moments dispersed in a nonmagnetic matrix are separated by relatively large distances. It was more recently concluded by Gupta, Cheng, and Beck[13,14] that the above condition for a magnetic contribution to γ is often met in concentrated alloys with a complicated magnetic structure, involving the superposition of both ferromagnetic and antiferromagnetic interactions. As the magnetic data show, such alloys may exhibit either long-range ferromagnetic spin order with a superimposed "parasitic" (short-range) antiferromagnetism or vice versa. In either case, the positive and negative exchange interactions may lead to approximate local cancellation of the resultant field in many small volume regions and, thus, the condition of a sufficient number of spins being located in a near-zero field environment may be satisfied.

The specific-heat results obtained in the present work with alloy $Ni_{0.48}Cu_{0.52}$, after cooling to helium temperatures in a magnetic field of 14 kOe and measured both in the presence (m m) and in the absence (m) of a magnetic field, are shown in Figs. 1 and 3, and Table I. It was found that the measured γ value is considerably reduced by magnetic cooling, particularly when the magnetic field is applied also during the measurements. It is, therefore, clear that the measured γ value for this alloy, and presumably for other alloys of a similar composition, does have a magnetic component. Thus, in these cases, the experimentally determined γ values are not representative of the electronic specific heat and they cannot be used to derive the band structure of Cu-Ni alloys with 0.45 Cu or more. The same may be also true for the very large γ values obtained for the fcc Mn-Cu alloys by Zimmerman and Sato.[17] On the other hand, the strongly ferromagnetic Ni-Cu alloys, up to 0.30–0.40 Cu, presumably have no "parasitic" antiferromagnetism, and the γ values for these alloys may be considered as true electronic specific-heat coefficients. Figure 5 gives the γ values from specific heat determinations by various investigators for Ni-Cu alloys. The dashed line in Fig. 5 shows schematically the electronic specific-heat coefficients, as expected on the basis of the simple band-model interpretation of the saturation magnetization data referred to above, with a γ value approximately equal to that for Cu at Cu contents above 0.55 and with the measured γ values up to 0.40 Cu. Although the measured γ values above the dashed line do not truly represent the density of states because of the magnetic contribution they include, the presence of magnetic moments does require an incompletely filled d band, even at Cu contents exceeding 0.55. Because of the d-band contribution to the density of states at the Fermi surface in such alloys, the true electronic specific-heat coefficients must lie at least somewhat above the dashed line. The formation of magnetic clusters in these alloys is likely to be associated with local variations in chemical composition in small volume regions. Such variations would be expected for statistical reasons even in an ideally random solid solution. Thus, local Ni-rich regions with lower than the average electron concentration may quite possibly give rise to magnetic moments and to the magnetic contributions to the measured γ values in alloys with average Cu contents higher than 0.55.

The results for the Ni-Zn alloys, although less detailed, appear to be generally similar to those for the Ni-Cu alloys. It is probable that the high γ value for $Ni_{0.74}Zn_{0.26}$ also comprises an important magnetic contribution, since the ferromagnetic exchange interaction is most likely quite weak at this electron concentration. The Al, Si, and Sb alloys with Ni show relatively little variation of γ with concentration within their somewhat limited solubility range.

ACKNOWLEDGMENTS

The authors wish to thank Dr. N. Pessall for his help with the measurements using a magnetic field. The work was supported by a grant from the National Science Foundation.

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