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Low-temperature behavior of Ni_3Al alloys near the spin-fluctuator–ferromagnet phase boundary

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The heat capacity C of two alloys of the composition $Ni_{73.75}Al_{26.25}$ (alloy IV) and $Ni_{76.41}Al_{23.59}$ (alloy V) has been measured in the temperature range 1.5–20 K. Magnetization as a function of temperature and applied magnetic field has also been studied for these two alloys and three other alloys (alloys I, II, and III: $Ni_{74.75}Al_{25.25}$, $Ni_{75.00}Al_{25.00}$, and $Ni_{75.60}Al_{24.40}$, respectively) which had been studied calorimetrically earlier [Phys. Rev. B **39**, 7453 (1989)]. The C/T versus T^2 plot of alloy V is linear in the range 1.5–12 K but a barely discernible upturn exists for alloy IV below about 6 K. From Arrott plots magnetic ordering temperatures of 38.2 and 68.9 K, and spontaneous moments of 0.076 and $0.114\mu_B$/Ni at 5 K were obtained for alloys III and V, respectively. Alloys I, II, and IV, however, are paramagnetic down to at least 5 K. The Curie temperatures of the ordered alloys III and V, when determined and compared with previous results published in the literature, show a composition shift between our chemically analyzed samples and those measured on nominal composition alloys. The difference is thought to be due to a loss of aluminum by vaporization during the sample preparation. These results, taken together with our earlier results, show that for some compositions the upturn in the C/T plots of well prepared "Ni_3Al" alloys, which have a solid solution range from 72.5 to 77 at. % Ni, is due to spin fluctuations and not due to magnetic clusters. Furthermore, our results show, for the first time, that the electronic specific-heat constant and the upturn approach a maximum as the composition approaches the spin-fluctuator–ferromagnetic crossover point (75.1 at. % Ni) from either side in accord with theory.

I. INTRODUCTION

Recently the results of heat-capacity measurements in zero and applied fields up to 9.8 T, in the range 1.5–20 K, on three alloys of the nominal compositions $Ni_{74}Al_{26}$, $Ni_{74.25}Al_{25.75}$, and $Ni_{74.5}Al_{25.5}$ were reported.[1] That work was undertaken to examine the influence of spin fluctuations, which are known to be significant in exchange-enhanced paramagnetic and weakly itinerant ferromagnetic $Ni_{3\pm x}Al_{1\mp x}$ alloys (see Ref. 1), on the low-temperature heat capacity of these three alloys (referred to as alloys I, II, and III, respectively, in Ref. 1). As is well known, the paramagnon description[2,3] of spin fluctuations in nearly and weakly ferromagnetic materials and, more recently, the self-consistent theory of renormalized spin fluctuations[4,5] predict a $T^3\ln(T/T_{SF})$ contribution to the electronic heat capacity at temperatures T below T_{SF}, the characteristic spin fluctuation temperature. In a C/T versus T^2 plot, where C is the heat capacity, the logarithmic term gives rise to an increasing C/T with decreasing temperature, which saturates to $C/T \rightarrow \gamma$ as $T \rightarrow 0$, where γ is the coefficient of the linear term in the heat capacity.[3] Qualitatively, an increasing C/T with decreasing temperature also occurs in systems containing magnetic clusters.[6] However, in the latter case, C/T exhibits a Schottky-like anomaly before intercepting the $T=0$ axis. It was found in Ref. 1 that the C/T plots in zero field for the three alloys I, II, and III showed a gentle upturn beginning at temperatures near 10 K and extending down to 1.5 K, the lowest-temperature data point, similar to the results of de Dood and de Chatel[7] obtained much earlier. For alloys I and II, an applied field of 2.5 T had no effect on the heat capacity and the upturn was progressively suppressed at fields ≥ 5.3 T. On the other hand, in alloy III the upturn was completely suppressed in a field of 2.5 T and the heat capacity was reduced in the entire temperature range 1.5–20 K in applied fields. Although the zero-field data were explainable on both the spin fluctuation and cluster-based models (i.e., a fit based on either of the two models passed through most of the data points), the data in applied fields favored the former as the likely cause of the upturn in C/T plots. Taking that point of view, it was considered likely in Ref. 1 that the upturn in C/T plots may not exist across the whole concentration range of single-phase $Ni_{3\pm x}Al_{1\mp x}$ alloys which extends from 72.5 to 77 at. % Ni. That conjecture would be in conformity with the reports in the literature by Ho *et al.*[8] and Collocott *et al.*[9] in which only a linear C/T versus T^2 behavior is observed. Therefore, in the present work, we have measured the heat capacity in zero field between 1.5 and 20 K of two more alloys of nominal composition, $Ni_{73}Al_{27}$ and $Ni_{75.9}Al_{24.1}$ (henceforth to be referred to as alloys IV and V), respectively. These two compositions were chosen because they are quite distant from the critical composition for the onset of ferromagnetism which is near 74.5 at. % Ni as reported in literature.[10] Magnetization measurements as a function of field up to 5 T at several selected temperatures between 5 and 80 K were made on all five alloys, since alloys I, II, and III had not been examined in our earlier study.[1]

It is important to note at this point that the alloys I, II, and III of Ref. 1 were slightly richer in Ni content than given by their nominal composition (see Table I). From a comparison of magnetization data at few selected temperatures and fields with that reported in literature,[11] it was found that the susceptibility of alloy II was the same as that reported by Suzuki and Masuda[11] for $Ni_{74.5}Al_{25.5}$, which is close to becoming ferromagnetic. Alloy I was less magnetic than II but its susceptibility exceeded that reported for $Ni_{74}Al_{26}$ in literature. Alloy III, with a nominal composition of 74.5 at. % Ni, turned out to be ferromagnetic with a positive intercept on M^2 axis in an M^2 versus M/H plot (where M is the magnetization and H is the applied field) equal to that found for stoichiometric Ni_3Al which has a Curie temperature of 41.5 K and $\mu_s = 0.075\mu_B/\text{Ni}$.[10]

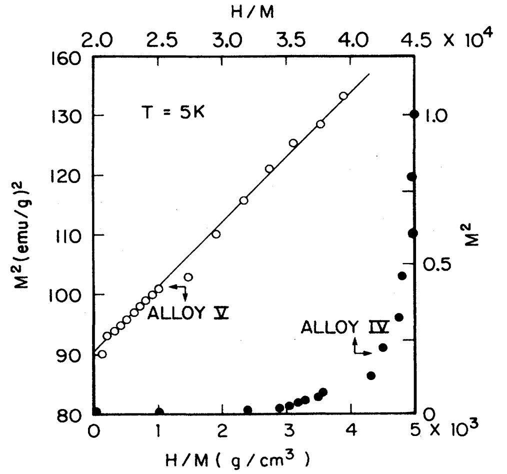

FIG. 1. Arrott plots for alloys IV and V at 5 K.

II. EXPERIMENTAL

The samples of the nominal compositions $Ni_{73}Al_{27}$ and $Ni_{75.9}Al_{24.1}$ were prepared at the Materials Preparation Center of the Ames Laboratory in the same manner as reported in Ref. 1, except that they were annealed at a lower temperature of about 1060 °C in an attempt to avoid the loss of Al due to evaporation, which is reported to take place at temperatures above 1100 °C.[10] In Ref. 1, the alloys were annealed at 1160 °C. However, even with a lower annealing temperature used in the present work, we find the alloys to be richer in Ni content than inferred from their nominal composition.

Because of the uncertainty in the actual composition, all five of the alloys were subject to chemical analysis. The aluminum and nickel contents were determined by a titrametric method. A second independent analysis of the nickel was made by using a gravimetric method. The agreement between the two methods for the nickel determination was excellent, the maximum spread between the lowest and highest values was <0.2 at. % Ni. The results are given in Table I.

Metallographic examination showed that both samples were single-phase materials. The heat capacity was measured in the same calorimeter with the same germanium resistance thermometer that was used in Ref. 1. The magnetization measurements were made using a Quantum Design SQUID magnetometer in fields up to 5 T.

III. RESULTS

Since the compositions of the five Ni_3Al alloys were well established, the magnetization of these alloys was measured as a function of temperature and field in order to establish their Curie temperatures and spontaneous magnetic moments. In Fig. 1, Arrott plots in the form M^2 versus H/M for alloys IV and V at 5 K show that the former does not order magnetically and that the latter has ordered. The Curie temperatures were obtained from Arrott plots near the ordering temperature; for example, see Fig. 2, where it is shown that the Curie temperature of alloy V lies between 65 and 70 K. A more accurate value of the Curie temperature is obtained by plotting the $y(M^2)$ and $x(H/M)$ intercepts of the linear portions of the Arrott curves in Fig. 2 versus the temperature, as illustrated in Fig. 3 for alloy V. A similar behavior as illustrated in Figs. 2 and 3 was found for alloy III. The Arrott plot results indicate that alloys I, II, and IV are paramagnets down to at least 5 K, and that alloys III and V (see Figs. 2 and 3) order magnetically at 38.2 and 68.9

TABLE I. Chemical analyses of the Ni_3Al alloys.

Nominal composition	Chemical[a] analyzed composition	Error[a] (at. %)	Alloy designation
$Ni_{73.0}Al_{27.0}$	$Ni_{73.75}Al_{26.25}$	0.08	IV
$Ni_{74.0}Al_{26.0}$	$Ni_{74.75}Al_{25.25}$	0.14	I
$Ni_{74.25}Al_{25.75}$	$Ni_{75.00}Al_{25.00}$	0.07	II
$Ni_{74.5}Al_{25.5}$	$Ni_{75.60}Al_{24.40}$	0.22	III
$Ni_{75.9}Al_{24.1}$	$Ni_{76.41}Al_{23.59}$	0.18	V

[a] The chemical composition given here is the average value from the composition calculated from the nickel analysis and the composition calculated from the aluminum analysis. The error is the difference from these measured compositions and the average value reported here.

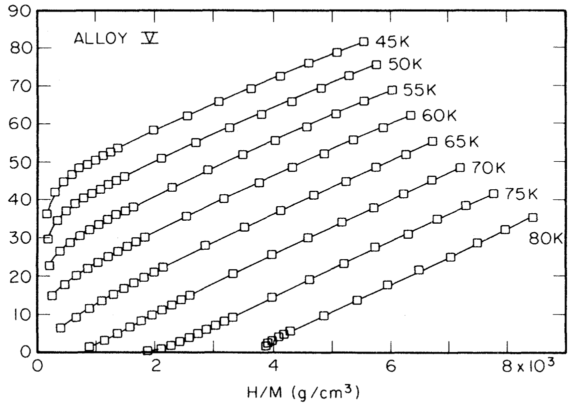

FIG. 2. Arrott plots for alloy V at eight temperatures between 45 and 80 K.

K with saturation moments of 0.076 and $0.114\mu_B$/Ni, respectively.

The composition dependence of the Curie temperature is shown in the upper portion of Fig. 4 along with the results reported in the literature. The chemical shift of our Curie temperatures is ~0.6 at. % towards richer nickel concentrations, which is slightly less than the difference between the nominal and analyzed compositions of our alloys, ~0.8 at. %, see Table I. We believe, and so do deBoer *et al.*,[10] that aluminum is lost by evaporation during high-temperature annealing. Thus the nominal compositions reported in literature are always too low in the true nickel concentration, and probably should be shifted by ~0.7 at. %. Based on our chemically analyzed alloys the onset of ferromagnetism at 0 K occurs at 75.1±0.2 at. % Ni, and not 74.5 at. % as reported in the literature based on nominal composition alloys (see Fig. 4).

Figure 5 shows the C/T versus T^2 plot for alloys IV and V. A linear behavior in the range 1.5–12 K is observed in the latter compound, while a mild upturn is observed for alloy IV in the same temperature range (see inset of Fig. 5). These results and those of Ref. 1 show the importance of stoichiometry and the associated magnetic state on the form of heat capacity in this series of alloys. The upturn is present at least up to composition $Ni_{75.6}Al_{24.4}$ (alloy III, Ref. 1, see Table I) which has a Curie temperature of 38.2 K. At higher Ni concentrations, the C/T plots are linear. The present results put the observations of Ho *et al.*[8] and Collocott *et al.*[9] in the proper perspective. The former reported linear C/T versus T^2 plots in the range 2–14 K for two separately prepared single-crystal specimens. From the weight analysis given by Ho *et al.*, both specimens turn out to have a Ni content slightly exceeding 77 at. %, the upper limit for single phase formation. Disregarding this anomaly, it is clear that the "Ni_3Al" specimens studied by Ho *et al.* are hyperstoichiometric (i.e., Ni rich), and like alloy V, their heat capacity does not exhibit any upturn. Collocott *et al.* measured the heat capacity of a nominally stoichiometric Ni_3Al between 0.5 and 15 K. They find some evidence of an upturn below 2 K but the data show appreciable error bars in this temperature range. We believe their sample composition is close to the limit where the upturn in C/T vanishes.

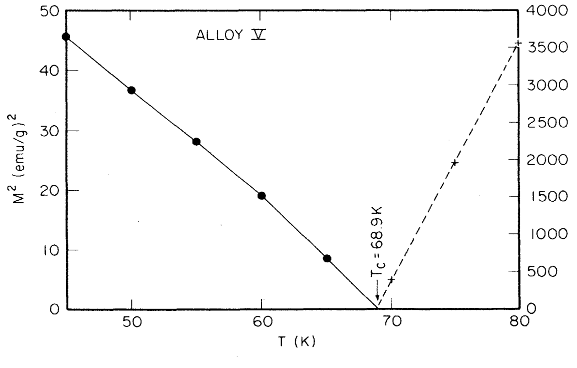

FIG. 3. M^2 (y intercepts from Fig. 2) vs temperature and H/M (x intercepts from Fig. 2) vs temperature for alloy V.

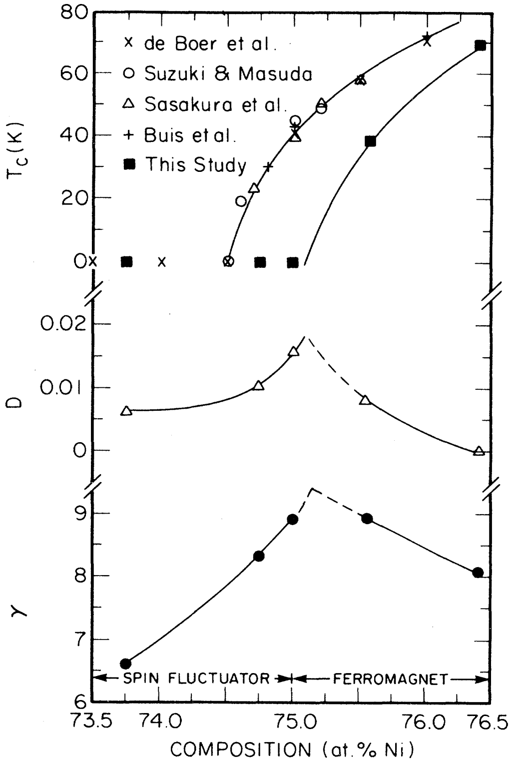

FIG. 4. The compositional dependence of the Curie temperature, T_c; the electronic specific-heat constant γ (in units of mJ/g atom K^2); the coefficient of the $T^2\ln T$ term, D (in units of mJ/g atom $K^4\ln K$) (see Eq. 2), which is a measure of the low-temperature upturn due to spin fluctuations. The Curie temperatures reported in the literature were measured on alloys of nominal compositions by deBoer *et al.* (Ref. 10), Suzuki and Masuda (Ref. 11), Sasakura *et al.* (Ref. 12), and Buis *et al.* (Ref. 13). See text for discussion concerning the composition shift of the Curie temperature.

As regards the physical origin of the upturn, the

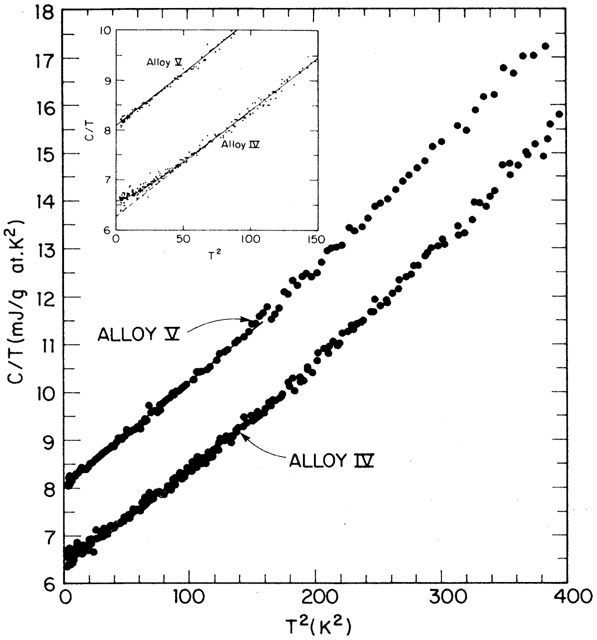

FIG. 5. C/T vs T^2 (where C is the heat capacity at temperature T) of alloys IV and V in the 1.5–20-K range. The inset shows an expanded version of the-low temperature results.

present results (as will be shown in a moment) support the conclusions of Ref. 1—that it is not likely to be due to the presence of magnetic clusters in the alloy matrix. If it is assumed for a moment that magnetic clusters are present in Ni-deficient alloys and cause the curvature in the C/T plots, then one would expect the curvature to be present in the Ni-rich alloys also. But a linear C/T plot in alloy V disallows such an assumption. A similar conclusion, i.e., the absence of magnetic clusters, had been deduced from a polarized neutron diffraction experiment on ferromagnetic $Ni_{75.9}Al_{24.1}$ long ago.[14]

A fit of the heat capacity data of alloy V in the range 1.5–12 K to the equation

$$C/T = \gamma + \beta T^2 , \tag{1}$$

where γ and β denote the electronic and lattice contributions to heat capacity, gives $\gamma = 8.07 \pm 0.01$ mJ/g atom K^2 and $\beta = 0.02158 \pm 0.00024$ mJ/g atom K^4. When compared with γ values of 8.32, 8.93, and 8.95 mJ/g atom K^2 for alloys I, II, and III, respectively, obtained in Ref. 1, we conclude that the coefficient of the linear term γ peaks around the composition for the onset of ferromagnetism (see Fig. 4). Ho *et al.*[8] obtained for their two single-crystal specimens, γ and β, values of 8.48 and 7.72 mJ/g atom K^2 and 0.024 and 0.021 mJ/g atom K^4, respectively. We conclude that one of their samples had Ni content slightly less than 76.4 at. % (the composition of our alloy V) and the other slightly more. We note that β exceeds the value of 0.01927 mJ/g atom K^4 corresponding to a Debye temperature of 465 K obtained from elastic constants[15] and inelastic neutron scattering[16] measurements. The slight discrepancy in β is probably due to additional magnetic contribution to the heat capacity in ferromagnetic alloys which effectively increases β.

The heat capacity of alloy IV shows a slight upturn at temperatures below ~6 K and, keeping in view the preceding discussion, we have fitted the data in the range 1.5–12 K to the equation

$$C/T = A + BT^2 + DT^2 \ln T , \tag{2}$$

where $A \equiv \gamma$. The values of the fit coefficients are $A = 6.59 \pm 0.01$ mJ/g atom K^2, $B = 0.0350 \pm 0.0002$ mJ/g atom K^4, and $D = 0.0062 \pm 0.0008$ mJ/g atom $K^4 \ln K$. In Ref. 1, the values of D for alloys I, II, and III were found to be 0.0106, 0.0161, and 0.0082 mJ/g atom $K^4 \ln K$, respectively.

IV. DISCUSSION

A consistent explanation of the heat capacity results on "Ni_3Al" alloys reported in the literature is possible on the basis of spin fluctuation model. Various authors have considered the effect of spin fluctuations on the heat capacity in nearly and weakly ferromagnetic alloys and have qualitatively given similar expressions for heat capacity.[2–5] The original paramagnon model[2,3] gives the following expression for heat capacity:

$$C = \gamma_0 T [m^*/m + \delta (T/T_{SF})^2 \ln T/T_{SF}] + \beta T^3 , \tag{3}$$

where m^*/m is the 0 K many-body mass enhancement, γ_0 is the electronic heat capacity constant determined from the band structure density of states, and βT^3 is the usual lattice contribution. The coefficient of the $T^3 \ln T$ term, δ, is proportional to $S(1-S^{-1})^2$, where S is the Stoner enhancement factor. For large S, δ goes approximately as S. Therefore, as one approaches the ferromagnetic transition from the paramagnetic side, i.e., increasing S, the magnitude of δ increases [see Fig. 4, where $\delta \propto D$—compare Eqs. (2) and (3)] and the upturn in C/T, due to $\delta T^2 \ln T$, should become stronger. A graphical depiction of C/T at low temperatures as a function of α is shown in Ref. 4, where α is defined as the product $I\chi_0/2$; χ_0 is the uniform susceptibility in the absence of the electron-electron interaction I. For ferromagnetism to occur, $\alpha = 1$. It is seen that C/T increases at low temperatures for values of α close to $\alpha = 1$ on both the lower ($\alpha < 1$, paramagnetic) and higher ($\alpha > 1$, ferromagnetic) side. For values of α slightly away from 1, both the magnitude of C/T and the upturn are predicted to be drastically reduced. This means that on the paramagnetic side, if the exchange enhancement of the alloy is modest, i.e., a small S, then the upturn due to the $\delta T^2 \ln T$ term would be negligible. This explains the barely discernible upturn in alloy IV, which has a susceptibility five times less than that of alloy I at 5 K. Similarly, on the ferromagnetic side, as the spontaneous magnetization at $T = 0$ K increases and the spin fluctuations give way to spin waves, the upturn in C/T would again vanish. It is likely that in alloy V ($\mu_s = 0.114 \mu_B$/Ni) the latter situation prevails. Thus, on the basis of the spin fluctuation model it is possible to explain, qualitatively at least, the heat-capacity results obtained on Ni-Al alloys around the composition Ni_3Al (see Fig. 4).

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